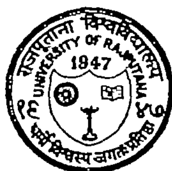
UNIVERSITY OF RAJPUTANA STUDIES

UNIVERSITY OF RAJPUTANA STUDIES

PHYSICAL SCIENCES

(including Mathematics & Engineering)



CONTENTS

1

ABSENCE OF L. F. PULSES IN THE DISCHARGE CURRENT FROM AN OZONISER

By

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[Abstract: The discharge current from an ozoniser is examined by oscillographic methods The results indicate that the discharge current consists of a sinusoidal current of th frequency of the exciting potential and the h. f. pulses of 1-5 kilocycles frequency The observation of Deb and Ghosh (1948) on the l. f. pulses in the discharge cu rent is therefore, not supported. The absence of l f pulses in the discharge current is shown to be in accord with the mechanism of ozoniser discharge proposed by Harris and von Engel (1951)]

INTRODUCTION

That the discharge current from the ozoniser has a component the frequency of which is very high compared to the frequency of the applied potential is well known (Warburg 1024). Kl mene Hinterberger and Hoffer (1937) pointed out that the h. f current consists of a great many closely packed unidirectional pulses rather than th h. f. oscillations as originally thought of The mechanism of these h f. pulses have been discussed in greater detail by Deb and Ghosh (1948) and very recently by Harris and von Engel (1951).

Deb and Ghosh (1948) from an oscillographic study of the discharge current classified the h f. pulses into two heads

(a) Group of pulses occurring during a part of the half cycle in which the individual pulses are separately observable. These are termed as l. f. pulses.

(b) Group of pulses in which pulses are densely packed and run into one another These are termed as h f pulses. Suppression of these h. f pulses under light causes Joshi-effect— Δ i.

However the frequency ranges of h f pulses and l f pulses have not been mentioned as also the capacity used to by pass h f. but not the l f pulses

The terms h f and l f pulses have been frequently used in the literature *on Joshi-effect without specifying their frequencies*. For example Prashad and Jain (1947) attribute decrease in the relative Joshi-effect, $-\%\Delta i$ with increased exciting potential to the predominence of l f *current which according to them is* comparatively insensitive to the production of Joshi-effect, $-\Delta i$. In the light of these facts it was considered desirable to determine the frequency ranges of the h. f and l. f pulses from an oscillographic study of the discharge current from an ozoniser

EXPERIMENTAL

The experimental arrangement is indicated in Fig 1 Alternating potentials of 50 cycles frequency were stepped up by a transformer (1.20) and applied to ozoniser containing purified chlorine at a pressure of 150 mm. The discharge current was made to flow through a resistance R = 15 000 ohms and the P D across the resistance R was applied to the vertical plates of a single beam *oscillograph (supreme 546)* and the discharge *current in dark was* studied at different applied potentials with and without a by pass capacity The oscillograms are reproduced (Plates 1–6).

DISCUSSION

The oscillograms of the discharge current in dark with and without by pass capacities at various exciting potentials indicate that the minimum capacity to by pass a part of the h. f. pulses is 0 005μF while a capacity of 0 025μF completely by passes the h f pulses and only a smooth a. c trace is obtained.

According to Harris and von Engel (1951) the total pulse time is about 2×10^{-4} sec. This gives the frequency of h f pulses *as five kilocycles. If the* pulses by passed by a capacity 0.005μF have a frequency of five kilocycles the frequency of the pulses by passed by a capacity 0 025μF but not by 0 005μF will have a *frequency* of approximately a kilocycle The pulses by passed by a capacity 0 025μF are essentially the h. f pulses It therefore, appears that the discharge current consists of a sinusoidal current of the frequency of the exciting potential and the h. f. pulses of frequency 1–5 kilocycles. The absence of l f pulses

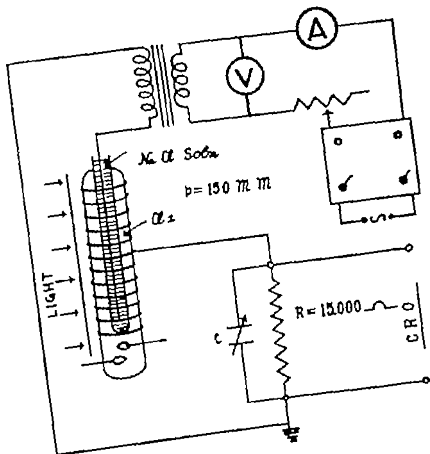


Fig 1



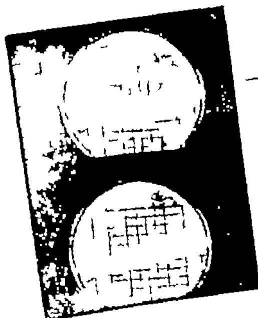
Exciting Potential $= 0.64$ kV

(a) Dark



(b) Dark with by pass capacity $= 0.005 \mu F$

Plate 1

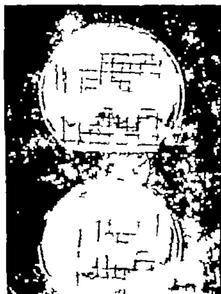


Exciting Potential $= 0.64$ kV

(a) Dark with by-pass capacity $= 0.025 \mu F$

(b) Light

Plat 2



Exciting Potential = 0 80 kV

—(*a*) Dark

—(*b*) Dark with by pass capacity = 0 005 μF

Plate 3



Exciting Potential = 0 80 kV

—(*a*) Dark with a by pass capacity = 0 025 μF

—(*b*) Light

Plate 4



Exciting Potential 0 80 kV

—(a) Dark



—(b) Dark with by-pass capacity = 0 005μF

Plate 3



Exciting Potential = 0 80 kV

—(a) Dark with a by-pass capacity = 0 025μF

Plate 4



Exciting Potential
=1 00 kV
—(a) Dark



—(b) Dark with a
by-pass capacity
=0 005μF

Plate 5



Exciting Potential
=1 00 kV
—( ) Dark with a
by pass capacity
=0 025μF



—(b) Light

Plat 6

having frequencies intermediate between the frequency of h.f. pulses and the frequency of the a. c exciting potential, is thus evident.

Deb and Ghosh (1945) have reported the presence of l.f pulses in the discharge current. These authors have reproduced oscillograms which show l.f pulses when the h.f pulses are by passed by a capacity Unfortunately these authors have not mentioned the capacity which by passed only the h f. pulses and hence nothing can be said about their observations.

Deb and Ghosh (1948) have also provided an explanation for l.f. pulses they claim to have observed. According to these authors "Electrons and ions produced by the discharge are urged towards the lectrodes but they are unable to produce continuous c rrent and are partly deposited as surface-charges and partly remain as polarised space-charge. The surface-charge and the space-charge together neutralise the externally applied field and the discharge stops. Which of the two surface-charge or space-charge is primarily determinative of the stoppage depends of course on their relative densities. But as the applied a. c. voltage increases in course of its cycle, the breakdown voltage is again reached overcoming the neutralisation effect of the surface and space-charges. There is again ionisation and again deposition of surface-charges and increase of space-charge the effect of applied field is again neutralised and the discharge again stops. The phenomenon may thus be repeated a number of times and continue till the rate of the increase of external field becomes slower than the rate of neutralisation of the same by increase of the surface and the space-charges. This staring and stopping of the discharge gives rise to the l. f. pulses.

On the above mechanism the l f pulses should occur on the increasing part of the a. c. voltage cycle on the otherhand h f. pulses (which according to Deb and Ghosh are due to the discharging of the surface-charges when th applied voltage is passing through its zero value) should occur wh n the applied voltage is passing through its zero value The oscillograms for the l. f. pulses (when the h f. pulses are by passed with capacity) reproduced by these authors indicat that the l. f. pulses appear on the same part of the voltage cycl where h. f pulses are also observed. their own observations are not in accord with the m the l. f. pulses they have proposed

According to Harris and von Engel (1951) "The glass walls act as condensers which are charged by the ionisation current flowing through the gas. When the field in the gas is sufficiently strong, an initial electron starting at the negative wall will cause an electron avalanche in the gas thus electrons are driven to the positive wall and positive ions to the negative one Positive ions, light and metastabl atoms will release further electrons (as in counters with insulated walls) and a series of avalanche develops. This increase in the number of electrons and ions and the corresponding rise in the current would only continue if the fields in the gas remained unchanged Because unlike charges collect on opposite walls a voltage drop develops across the glass walls. Since the applied potential is sensibly constant during the pulse time th p. d across and the field in the gas are thus gradually lowered. Consequently the rate of ionisation and current decrease and approach zero values. This accounts for their observation of h. f pulses near the peak value of the voltage at lower potentials. "At higher potentials the current pulse can be seen to occur during the whole time interval between successive peaks of the ed voltage However the polarity of the current pulses re- the same although the applied voltage changes sign This follows from the existence of wall charges field the field in the gas which is the difference between the instantaneous values of the applied and the wall charges field is always in the same direction and so the current must have the same polarity Further for an elem ntary area the number of pulses per half cycle cannot xceed peak applied voltage divided by the starting potential

It will be clear that the origin of h. f. pulses proposed by Harris and von Engel (1951) takes into account the starting and topping of discharge due to deposition of wall charges and the discharging of the wall charges the former according to Deb and Ghosh (1948) give rise to l. f. pulses while the latter gives rise to h f pulses. Thus the considerations of Deb and Ghosh (1948) are taken into account by Harris and von Engel (1951). Further the considerations of Harris and von Engel (1951) do not suggest the presence of l f. pulses in the discharge current. Thus the reported absence of l. f pulses in the discharge current is in agreement with the mechanism of h. f pulses proposed by Harris and von Engel (1951).

ACKNOWLEDGEMENT

Grateful thanks are due to Prof S S Joshi, Principal College of Science, Banaras Hindu University Banaras and to Prof M. F Soonawala, Head of the Department of Physics Maharaja's College Jaipur for their keen interest and encouragement.

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2

VARIATION IN THE PROPORTION OF H F CURRENT WITH APPLIED VOLTAGE IN OZONISER DISCHARGES

By

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[Abstract: Deb–Ghosh explanation of the decrease in the proportion of h f current is shown to be based on assumptions, the validity of which is questionable Based on the discharge mechanism of Harris and von Engel, an equation is derived which indicates a decrease in the proportion of h f current with increase in the applied voltage.]

Results of Warburg (1924), Joshi (1946) and Prashad and Jain (1947) indicate that the proportion of h. f current decreases as the applied voltage is decreased

Deb–Ghosh (1948) have derived an equation which indicates a decrease in the proportion of h. f current with applied voltage If f is the percentage of h f current in the total discharge current M the extinct voltage (at and below which discharge stops), V the peak value of the applied voltage then

$$\frac{df}{dV} = -\frac{kVm - M}{(V - Vm)^2}$$

where Vm is the threshold potential and k is a constant depending on the capacity system in ozoniser and is less than 1

The above derivation is based on the following assumptions

( ) h f pulses are produced by the neutralisation of surface-charges when the applied voltage is passing through its zero value

(*i*) The h f current is proportional to (kV −M) which is the opposing voltage set up by the surface-charges and

(*iii*) The total current is proportional to (V −Vm

On the basis of Deb-Ghosh mechanism pulses should always occur when the applied voltage is passing through its zero value Oscillograms of the discharge current and the applied voltage reproduced by Harris and von Engel (1951) indicate that at lower applied voltage the pulses occur at the peak value of the applied voltage while at higher applied voltages the pulses occur during the whole time interval between the successive pulses.

The current pulse on the discharge mechanism of Deb-Ghosh depends on $\frac{de}{dt}$ where e is the electronic surface-charge. The h f pulses occur when the applied voltage is passing through its zero value. At larger applied voltage the surface-charge is large The rate of change of surface-charge is therefore large The pulses should, therefore occur together or/and the pulse size should increase with increased voltage. The clustering of pulses has not been observed Further th average pulse height and its duration do not change appreciably with applied voltage (Harris and von Engel 1951). It will thus be seen that the assumptions (*i*) and (*ii*) are not justified. The ozoniser discharge can be regarded as a positive and negative point discharge (Glocker and Lind 1939) and is similar to wire in cylinder type of discharges The discharge current I, for wire in cylinder type of discharges is given by the equation (Loeb 1939)

$$I = C\,V\,(V - V_m) \quad \ldots \quad \ldots \quad \ldots (1)$$

where V is peak value of the pplied voltage V_m the threshold potential and C is a constant depending on th nature of the gas, its pressure and the geometry of the ozoniser tube The discharge current cannot therefore be taken as only proportional to $(V-V_m)$ as has been assumed by Deb-Ghosh.

In our opinion the discharge mechanism of Harris and von Engel accounts well for most of the known facts about ozonizer discharges. The mechanism can briefly be stated as follows —

A pulse starts when the fields in the gas which is the difference between instantaneous values of the applied and the surf ce-charge fields exceeds a critical value depending on the pressure and the nature of the gas. Each pulse is associated with a discharge covering a small lementary area In addition each pulse is accompanied by a change of surface-charge which may be partial only and need n

For low applied fields when there is only one pulse per half cycle this single pulse originates from that elementary area which has the lowest starting potential at that time. The next pulse originates from a different area because their starting potential may change

At larger applied fields the pulse would only partially discharge the areas and the wall charge field would change in steps. This would explain why the pulses have the same sign whether they occur before or after zero applied field It also accounts for the constancy of the average height of the pulses Taking the starting potential and the average size of an area as being constant, the change of surface charge is proportional to the starting potential. Also for an elementary area the number of pulses per half cycle cannot exceed peak applied voltage divided by the starting voltage However the number of pulses observed are very much larger than this which suggests that a number of elementary areas was being discharged.

Also the wall charge field for an area will not remain constant between two pulses because discharges in the neighbour hood as well as surface condition may change its value Further discharges along the inner surface would occur if the potential difference between two adjacent sites exceeds the corresponding breakdown value "

On the basis of the above mechanism the number of h. f pulses is equal to $n\frac{V}{V_m}$ where n is the number of elementary areas discharged, V is the peak applied voltage and V_m the threshold potential. The average pulse height do not change appreciably with applied voltage (Harris and von Engel 1951) If k is the current per pulse the h. f current, $I_{h.f.}$, is given by

$$I_{h.f.} = k.n.\frac{V}{V_m} \qquad \text{.....(2)}$$

The total current I is given by equation (1)

$$f = \%\text{ of h f current} = \frac{I_{h.f}}{I} \times 100$$

$$= \frac{k.n.\frac{V}{V_m} \times 100}{CV(V-V_m)} = \left(\frac{k.n.100}{C}\right)\frac{1}{V_m(V-V_m)}$$

For a given ozoniser tube containing a known gas at the same pressure Vm is constant if other external conditions like irradiation, ionising radiations etc. are unaltered

$$\frac{df}{dv}=\left(\frac{k.\ n.\ 100}{0\ \ Vm}\right)\times\frac{1}{(V-Vm)} \qquad .. \quad (3)$$

Equation (3) gives the variation of the proportion of h. f current with the applied voltage. $\frac{df}{dv}$ is a negative quantity indicating that the proportion of h. f. current decreases with increase in the applied voltage

Grateful thanks are due to Prof. S S Joshi, Banaras Hindu University and Prof. M F Soonawala, Maharaja's College, Jaipur for interest and encouragement.

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3

NEGATIVE JOSHI EFFECT IN RELATION TO APPLIED VOLTAGE

By

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Abstract :—The explanation offered by Khastgir and Setty for the inhibitory action of applied potential on Joshi Effect, in light of Deb and Ghosh's theory for the phenomenon, was examined critically a few limitations of the theory were also pointed.

Detailed investigations of Professor Joshi and coworkers on Joshi effect viz. a photoreduction (Δi) of the rms value of the discharge current and the associated (h f) pulses observed on a cathode ray oscillograph, have established that the effect Δi is inhibited by large applied voltages, this appeared to be a general characteristic of the phenomenon. Recently Khastgir and Setty[1] explained the variation of Δi with applied potential in terms of an interesting mechanism developed by Deb and Ghosh[2-3] at a suggestion due to Professor S K Mitra. The present communication reports a few remarks on the above

According to Deb and Ghosh, the pulses detected on a cro are of two types low (individual and separately observable) and high (densely packed and running into one another) frequency pulses. It is suggested[2-3] that *(a)* low frequency pulses are due to stopping and starting of discharge by the surface and space-charges of electrons and ions and by the increasing alternating fields respectively *(b)* h f pulses are manifestations of sparks resulted from *neutralisation of surface-charges of opposite signs (f electron and positive ions) formed on the two glass electrodes* and *(c)* irradiation liberates electrons from the electrode wall to reduce the corresponding surface-charge density nd therefore, the h. f pulses hence the Joshi effect

The following may be mentioned

(i) Khastgir and Setty[1] state that electrons which move with much higher velocity reach the anode side and deposit a negative charge on the glass surface and the positive ions which hardly move away from the anode form a positive space charge near the negative space charge on the inner glass of either electrodes This does not seem to be correct from the following calculations which sh w that for the interelectrode distances of the systems giving large Joshi effect, the formation of positive ionic space charge in the gas phase is negligible by the time the alternating field acquires after th peak value its subsequent zero value at which point only neutralisation of opposite charges, resulting in h. f pulses is maximum and complete For the studies of Δ_i in oxygen Mohanty used an ozoniser of interelectrode separation of 1 75 mm, th threshold potential was 2700 volts, the peak value being ~3800 volts. Assuming that th mobility of positive ions is 1·0 cm/sec[2] and employing the formula[3] for the velocity f ions in a system composed of concentric cylinders it can be shown that the velocity of ions at the peak value would be ~3000 cm/sec and that the ions would cross the interelectrode spacing in 6×10^{-5} sec *i.e* in less than 1/80 of the time of the quarter ycle It therefore follow that the positive ions created t the peak value of a. c potential are swept out completely towards the cathode much before the time by which the alternating potential falls to zero. Similar calculations for external sleeve excitation in iodin vapour and other media support this deduction. This circumstance will be more facilitated the greater is th pplied potential These considerations are in agreement with th views of Deb and Ghosh (*cf* b) and suggest that th later statement also made by Khastgi and Setty *viz.* "with increasing voltages, it is vident that the positive ions will move a little further nd their distance from the negative space charge will slightly increase necessitating a slight increase in th voltage necessary for a discharge or discharges to pass between the negative surface charge and the positive ion is incorrect. Further the curve C of their Fig I should therefore be parallel to x-axis unlik that represented.

In this connection, it may be pointed out that Khastgir and Setty represented the surface charge collected at either electrodes in dark and under light as a function of applied voltage by the

curves A and B Since alternating potentials were employed it would have been appropriate to mention the voltage breakdown peak or subsequent zero value of the alternating cycle at which the surface charge represented on y-axis was collected at either electrodes. (*If it* were to be the breakdown value *for a fixed* pressure and interelectrode separation the surface charge would be the same whatever the externally applied (effective) potential may be in this case the curve A runs parallel to x-axis. If the peak value were to be taken into account, the curve B would coincide with A since at that instant light cannot liberate electrons from the anode. However if the circumstances at the zero value are visualised, the scale on x-axis appears to have no meaning.)

(*ii*) Khastgir and Setty point out that "at higher voltages however the increased series resistance of the discharge circuit corresponding to decreased internal resistance of the discharge tube makes the pulses highly damped The amplitude of the pulsatory current is therefore much less at higher voltage so that ultimately the effect of increased damping predominates and the photoreduction eventually falls off with further increase of applied voltage" That the decrease of internal resistance *i. e* the production of enhanced number of electrons and ions, causes a reduction in the pulses which according to Deb and Ghosh are due to surface-charges, does not appear to be logical. It is difficult to visulise how the increased number of ions and electrons could not form the surface-charges In fact, at large fields the entire current trace is usually superimposed completely with h. f. pulses further the current (observed with suitable detectors) correspond ing to l f and h. f pulses as also their entirety continuously increased with voltages beyond those values which decreased the Joshi effect[6]

(*iii*) As far as the variation of Joshi effect with applied voltage is concerned, a distinction between the ozoniser discharge tubes and others fitted with adjustable sleeve electrodes is made While in ozonisers the Joshi effect after a maximum value decreases gradually in sleeve tubes Δi varies similarly and vanishes altogether with continuous rise of voltage In this connection the present authors wish to emphasise that this distinction is not universal though not incorrect The magnitude and range

(voltage) of occurrence, of Δ even in ozonisers depend upon *inter alia* the surface condition. In one series of experiment with ozonisers some of which were degassed for the removal of adsorbed water vapour layers Saxena and Bhatawdekar observed that Δ in iodine vapour enclosed in degassed vessels was as much as 97% near V_m (385 volts 50~) and decreased to zero with an increase of 440 volts above V_m while in nondegassed vessels Δ was about 60% near V_m and could be detected as mentioned by Khastgir and Setty over a wide range of applied potential (It appears therefore that the results obtained by these authors refer to ozonisers of which the preadsorbed layers of H_2O CO_2, etc are not removed prior to the introduction of iodine vapour into the system, this is a very fundamental precaution one has to take into account especially while dealing with a phenomenon concerned with surface-changes)

(*iv*) Khastgir and Setty further remark that in case of sleeve discharge tubes "the amount of negative surface charge will decrease steadily till at some high voltage the surface charge will not be adequate for the discharge to take place between it and neighbouring positive ions" Actual observations do not support this statement. Even with sleeve excitation, at large V sufficient enough to inhibit Joshi effect, h. f pulses much more in number than detected at low V were noticed. In this connection, it may be interesting to recall the following sentence from a published paper by Jatar who has reported for the first time the results in iodine vapour *under sleeve excitation* 'Oscillograms correspond ing to large potentials show that 'the number of h f pulses increased markedly rapidly' Since according to Deb and Ghosh h. f. pulses are due to neutralisation of surface charges the above observation contradicts the suggestion due to Khastgir and Setty that at large V in sleeve tubes surface charges are not formed.

(*v*) It may be pointed out that Khastgir and Setty maintained throughout a view that whenever h. f. pulses were produced in a system Δi could be detected and *vice versa* Oscillographic studies over a wide range of experimental conditions show that the production of pulses on cro is a characteristic of the discharge while Δi *viz.* their suppression under light, is but observed under conditions favouring sorption. For example at enhanced *tempe-*

ratures, say 200 C the current trace under known conditions of pressure and potential, was completely full of h. f. pulses however no Joshi effect could be detected.

A very significant observation of professor Khastgir may be recalled "Over a definite voltage range above V_m (*i.e.* V_m to V_n, Fig 1) the discharge will be completely stopped on irradiation and the pulses will be quenched altogether The photoreduction of the pulsatory current will then be given by the current in dark This indicates that in above voltage range the percentage reduction of current under light amounts to 100 Essentially similar result *viz.* 100% Joshi effect, was recorded in chlorine air mercury vapour etc. employing detectors like microammeter vacuo-junction, etc [18] This would suggest that under these conditions light inhibited not only the h. f pulses but also the l f pulses. The suppression under light of these last is not warranted from the above mechanism due to Deb and Ghosh since in the course of increasing region of the alternating voltage from breakdown to above values, in which time the l f pulses are produced (cf *a*) external light cannot stop deposition of or liberate electrons from the anode electron emission from the anode is incomprehensible. Enhanced release of electrons from the cathode leading to further electron avalanches, will on the other hand produce more pulses.

It may not be out of place to consider in some detail the suggestion (*c*) of Deb and Ghosh regarding the origin of Joshi effect. In one half cycle *i e* when one electrode is negative and the other positive electrons are deposited on the anode and the positive ions on the cathode When the alternating potential acquires its zero value light depending upon its intensity releases some number of electrons from the electrode which is hitherto as the anode the other electrons remaining on the wall as surface-charge it is contemplated neutralise with positive ions It is worthy of enquiry of wh t will happen to the electrons released by light These also should neutralise with positive ions rather early than the surface electrons unreleased by light. This suggests, therefore that the number or/and heights of the h.f pulses determined by the amount of neutralisation, should be the same in dark and under light.

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(*Not added to the proof*)

A copy of the manuscript *of* this paper has been sent, on 7th Nov 1952, to Prof. Khastgir to which he replies to one of us (N A. R.) that as a result of the calculations and other factors mentioned in the communication, he has altered his views regarding the production of pulses and especially the possibility of positive ion accumulation in the gas phase in a low frequency a.c disch rge An account of his current views based on the 'streamer mechanism of Loeb and Meek, has been published late in *Science & Cultu* (F b issue 18, 394, 1953). It may be remarked that th ideas regarding the 'streamer' mech nism of spark discharge with unidirectional potentials are inapplicable to discharge with low frequency lternating potentials The details of the arguments underlying this statement will be published elsewhere

4

INFLUENCE OF SORPTION OF GASES ON CONDUCTIVITY IN A/C SILENT ELECTRIC DISCHARGE

By

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[Abstract: Chemisorption of iodine bromine and water vapour on glass surface as a determinant of the current *i* passing through an ozoniser excited by 50 cycle potentials, was investigated in acid treated and untreated discharge tubes In thesis last, *i* decreased markedly rapidly and attained saturation within 5-12 mins. The rate of decrease of *i* obeyed a power-time law Acid treatment of the vessels *i e.* removal of surface alkali affected markedly the variation of the conductivity presumably due to a change in the sorption.]

INTRODUCTION

The effect of sorbed gases on photo and thermo-electric cur rents has been well investigated It was observed as early as 1693 by Cantor[1] and later (1899) by Knoblauch that substances when exposed to ultraviolet light, lost some negative charges Chrisler found that this phenomenon *viz.* photo-electric effect, could be eliminated completely in certain cases by the removal of occluded gases. When zinc was freed from all active gases by scrapping it in vacuum no photo-electric ffect in the metal appeared evident. Similarly when all occluded gases from potassium are removed the photo-electric effect disappeared entirely Essentially like results were obtained by number of other investigators. While the data of the above workers emphasised the favourable influence of adsorbed gases on photo-electric effect, contrary findings indicating

their inhibitory action on electron liberation from metal by light, were also recorded Thus Stoletow found that the photo-electric effect from platinum increased when the adsorbed gases were removed by heating it to 200°C t 700°C the effect was twice that at laboratory temperature Similar data were obtained by Varley and Unwin [19] It was shown that the photo-electric sensitiveness after emission of occluded gases was definitely larger than the effect noted before the expulsion of the gas. The above contradictory results received explanation from th findings due to Paech that the photo-electric effect of a metal was dependent upon the nature of the gas occluded or adsorbed such as hydrogen, oxygen, carbonmonoxide etc. It h s been emphasised by Hallawachs that electropositive gases cause an increase and electronegative gases, a decrease Further a distinction was made between the gas *absorbed* within the body and those *desorbed* on the surface of the metal Adsorbed gases retard the escape of electrons, whil absorbed gases aid the liberation of electrons, apparently by causing some internal agitation. These views are substantiated by the data on thermo-electric effect This phenomenon was well investigated by Langmuir and others. It was noticed that thermo-electric effect of tungston was markedly inhibited by sorption of oxygen and not restored even when the metal was heated to >2000°C to exclude the adsorbed gas the irreversible diminution of thermo-electric effect of W by oxygen was attributed to the formation of a compound between W and 0 Similar data were obtained by Richardson and Bosworth Much advancement in the studies of sorption was achi ved by the fundamental investigations of Langmuir According to him, there exist a fixed number of tomic gr ups or sites per unit area of the solid surface on which alone adsorption of a gas atom or a molecule can take place (*vide i f a*) These adsorbed atoms depending upon th ir electron affinity retard as mentioned by Hallawachs [19] the escape of electrons

While photo and thermo-electri currents nd the influ ce thereon of adsorbed films received much ttention, the variation of the discharge current with th surface nature of the lectrodes especially with solid dielectric material was not investigated. It has, however been mentioned that th discharge current and the mechanisms responsible therefor are markedly dependent upon the workfunction of the cathode chiefly the gases adsorbed on it This factor has now been investigated in some detail.

THEORY & METHOD OF INVESTIGATION

In general there are three processes which occur when a gas is brought in contact with a solid absorption diffusion and adsorption.[illegible] The phenomenon of absorption refers to the intake of gas by the entire bulk, while diffusion deals with the passage of gas atoms or molecules through the intermolecular capillaries of the solid substance[illegible] In the last process, adsorption a known quantity of the gas is taken up by the surface and surface alone of the solid These three phenomena are summarised by a single name 'sorption [illegible] Among these adsorption is of marked importance and the only process which is found to occur at ordinary temperatures, with substances like Cu Al Au Ag, Pt, glass, etc which are in common use as electrode material it is the adsorption process only that is referred to in this paper

Adsorption is principally of two types the instantaneous and slow processes. When a gas is allowed to come in contact with a clear solid subst nce a known amount of it, depending upon the temperature nd pressure thereof is taken up instantaneously[illegible] it is said that in this case the gas exists in the form of multilayers[illegible] of molecules held by some nonspecific forces.[illegible] This process is also referred to as phy ical, multimolecular or van der Waal s adsorption This is followed by the slow process the maximum time necessary for the attainment of saturation is of the o der of a few hours to years.[17] The large time recorded was not due to slow diffusion, since the corresponding constants as shown by Herbert[illegible] varied characteristically with pressure It was further emphasised[illegible] that the long intervals noted at the saturation time in the slow process were not untenable from the following theoretical considerations. It is surmised generally [illegible] following Langmuir that there are a definite number of atomic groups or sites per sq cm. of solid surface on which sorption of a gas particle can take place it is further assumed that these atomic groups are unable in their normal condition to adsorb and require first to be *activ ed* before they actually combine with or adsorb a molecule or an atom (the anology was taken from the formation a chemical compound by the union of two or more atoms; this mechanism is therefore referred to as Langmuir s well known chemical theory of sorption) the necessary energy being obtained from the excited atoms or molecules arriving from the gas phase to the solid surface

due to thermal movem nts. It has been stated above that no sooner the gas is introduced into th system containing nude surface van der Waal s sorption in which the gas exists in the form of multimolecular layers akin to those of liquid phase takes place instantaneously A gas atom or a molecule with enhanced excitation energy should therefore dive into these layers reach the Langmuir site and transfer its nergy to this last. The rate of sorption depends upon the probability of the excited atoms or molecules reaching the solid surface containing free Langmuir sites; sorption attains saturation when these last are completely occupied. For obvious reasons this process is also referred to as Langmuir adsorption chemisorption or activated adsorption.

As mentioned above the rate of chemisorptions depends upon the probability factor regarding the accessibility of th excited gas particles to the solid rface [*1] Under discharge the population of excited atoms or molecules and presumably their reaching the surface are exceedingly marked on account of this sorption under discharge is expected to be very rapid, as actually observed [21-24] (*vide infra*) From this it follows that whatever processes that occur under ordinary conditions and during discharge refer to one and the same phenomenon *viz.* chemisorption or Langmuir dsorption.

The influence of Langmuir adsorption on the electrical conductivity of a gas was now investigated. For this purpose the discharge tubes were outgassed for the removal of adsorbed gases and a known quantity of a gas was introduced therein and excited by a fixed potential. The variation of its current was studied at regular interval of time during the progress of sorption under discharge.

EXPERIMENTAL

Description of the discharge vessels Siemen s type discharge tubes were used. These were pecially mployed for the present tudies on account of the fact th t no metal surface would come in contact with th gas under investigation. It is wellknown that the data on sorption of a gas from discharge tubes are highly

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Whenever the rate of sorption is mentioned. t refers to the slow p ocess only and not to the other kind f sorption *viz* physical or van der Waal adsorption; the rate of instantaneous process is inconceivable.

complicated by loss or gain at the metal surface The use of the Siemen's tubes is however open to the objection of allowing slight liberation of gases or/and formation of certain surface compounds due to the electrolytic nature of the conduction of elecricity through glass under conditions at which the experiments reported herein were carred, the above processes were assumed to be minimum *(vide infra)*

The following are the dimensions of a typical one of the discharge tubes used

Outer diameter of the outer cylinder	20.5	mm
Inner "	18 0	"
Outer diameter " " inner "	12 0	"
Inner " " " "	10 0	"
Length of the cylinders (verage)	420 0	"

Some of the ozonisers were immersed in chromic acid for about 24 hours and then washed repeatedly with boiling distilled water These were referred to as acid treated discharge tubes. The others were employed as prepared *i. e.* without acid-treatment and regarded as untreated vessels.

Outgassing Temperatrue —The surface of the discharge tubes was freed from preadsorbed gases by the following process. The vessels were enclosed in an asbestos chamber fitted with heater coils (Fig 1) They were maintained at a temperature of $\sim 210°C$ for about 15 hours the temperature wa deliberately kept $< 250°C$ for the reasons mentioned below The evolved gases were condensed in a trap (L, Fig 1) connected serially to the discharge tubes and cooled by liquid air This process was shown experimentally to be appropriate for the removal of gases from glass urface by Razauk and Salem.[8] A sample of soda glass was outgassed for 15 hours at 25 100 200° and 300°C and adsorption *isotherms of water vapour on the degassed surface were determined.* The data showed that the amount of gas adsorbed for a known relative pressure increased with outgassing temperature upto 200°C no variation therein was noticed as temperatures $> 200°C$ This suggested that outgassing at 200°C for 15 hours was efficient for the removal of adsorbed layers from glass surface this procedure was in agreement with the findings of Sherwood and others[36,37] who

showed that when glass was outgassed at increasing temperatures surface layers mainly H_2O and CO_2 were evolved at 200°C. At higher temperatures, > 300°C continuous liberation of gases was however noticed presum bly due to diffusion from the interior or/and a change of the constitution, on account of decomposition, of the glass. In the present series of experiments connected with adsorption process which is related with surface changes, it is aimed not to complicate the affairs with other processes *viz.* diffusion and bsorption " the interior of the solid is left undisturbed and the changes are confined to the removal and replacement of superficial layers "

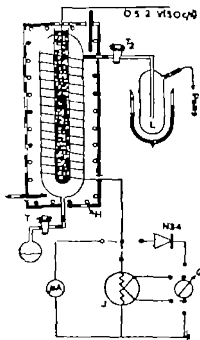


Fig 1

Experimental set up for the investigation of the va iation f the Discharge current with Chemisorption

(H Heater coils; L Liquid air trap; V J Vacuo-junction; IN34 : Crystal; for the details of the connections, cf Ref. 32.)

Working Voltage —The discharge tubes were excited by *alternating potentials of 50 cycles and the current was measured* by a micro-ammeter vacuo-junction or a crystal detector The details of these were given in a number of communications,[25-30] hence they were not reiterated here

The ozonisers were worked at potentials just near the threshold potential V_m the significance of which for the reacti ns under discharge in general, and for the phenomenon Joshi effect in particular has been emphasised by Professor Joshi,[29] It is found by the extrapolation of V i characteristi curves (Fig. 2) to the potential (V) – axis. Thus for water vapour (p=31 mm Hg 30°C) V_m was 0.60 kV and the potential employed for the studies was 0 68 kV

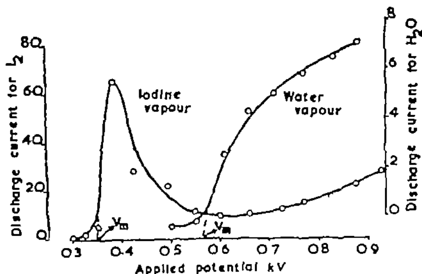


Fig 2

Determination f the Threshold Potential w ter and iodin vapou

While using the ozonisers, the following may be taken into consideration —

When pure hydrogen was exposed to electrodeless discharge in glass vessels in which electrolytic currents were maintained a *few condensible products were obtained* [31] spectroscopic studies revealed that these last consisted of water and the corresponding decomposition products[32] In a discharge in pure hydrogen, the

source of oxygen appeared curious This received satisfactory explanation from the consideration that glass was to be regarded as a solution containing Na_2Sio as electrolyte. Of the radicals liberated at the electrodes under discharge Sio_3 at the anode would breakdown into SiO and oxygen atoms which combined with hydrogen molecules to form water Similar products like carbon monoxide oxides of nitrogen etc were noticed with oxygen, nitrogen, etc. These evolved gases will naturally complicate the data on sorption and allied phenomena.[38]

The formation of certain surface compounds under discharge is known. Rodebush and Klingelhoeffer[41] observed a white deposit on the glass walls when chlorine was subjected to an electrodeless discharge and attributed it to a compound formed between Cl atoms and the constituents of glass. Kellner[43] obtained a similar compound when bromine vapour was exposed to ozoniser discharge. Ludeking[44] estimated the amount of NaI/NaIO formed in iodine vapou discharge During th course of certain experiments carried out with a view to explain the observed disparity in the influence of ageing on Joshi effect in water vapour in acid treated and untreated discharge tubes[31] Ratnam and Devi[41] observed by qualitative methods that when water vapour w s energised in ozoniser tubes compounds like NaOH were formed.

The reactions leading to the liberations of gases and the formation of certain surface compounds under discharge are essentially due to th electrolytic nature of conduction of electricity through glass[44] Professor Joshi[46] has shown that in general, the rate of a chemical reaction und r discharge is determined by th *potential diff rence (V V_m) where V is th* applied voltage mployed for studying the reaction It f llows from this that th smaller th difference ($V-V_m$) *i. e.* th nearer the potential to V_m the less marked is th rate of the reaction. The voltage employed for the present studies was maintained very near to the threshold potential such that th bove changes would be minimum,

Furthermore this would facilitate th studies of discharge mostly concerned with the surf ce of the electrodes, since it was shown in th following communication[44] that at potentials near V_m, the mechanisms related with the cathode *e. g* the liberation of electrons therefrom by positive ionic bombardment (γ) and photons ($\mu\delta g$) was predominant, while at large $V>V_m$ the other

processes unconnected with the surface and concerned with the gas phase (β) played an important role in the maintenance of the discharge.[47]

Gases investigated.—In the present investigation, water iodine and bromine vapours were studied. Water vapour was obtained from pure liquid water kept in a small bulb connected serially to the discharge tubes through a stop-cock T_1 (Fig. 1) its pressure was computed from the knowledge of the standard vapour pressure-data. Iodine and bromine vapours were obtained similarly from the corresponding solid and liquid enclosed in the bulbs

EXPERIMENATL PROCEDURE AND RESULTS

For the first series of experiments carried out with water vapour the ozoniser of the dimensions given above was used It was degassed and filled with water vapour (p=31 mm Hg 30°C) by opening the tap T_1 (Fig. 1) The system was excited immediately *i e. within 1/2 min after the introduction of the gas*, at 0 66 kV The variation of the discharge current at intervals of 30 secs was noted these data are represented graphically by curve

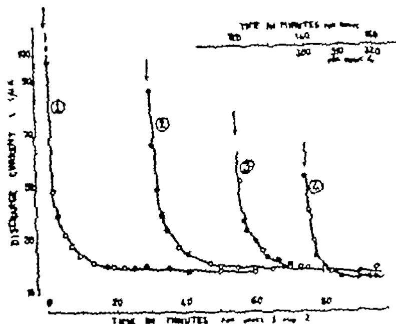


Fig 3

V riation f the Discharge current with time
(The rrow indicates the instant f excitation)

1, (Fig. 3.) After one set of experiments, the vessels were opened to atmosphere and later , *i.e.* after one day outgassed as described earlier They were cooled to the laboratory temperature slowly and filled with the same amo nt of gas (p_{H_2O} =31 mm Hg 30°C) Curves 2–4 (Fig 3) give the data obtained with predischarge intervals of 30 mins, 2 and 5 hrs. It was interesting to note that the conductivity was exceedingly large at the first instance of recording and decreased markedly rapidly with time Thus in H_2O vapour was 98 μamp t 1 min and 23 μamp at 9 min further exposure to discharge did not alter the conductivity appreciably Similarly in iodine vapour was 285 and 161 (relative units-galvanometer deflections) at 30 secs and 5 mins respectively (Curve 1 Fig. 4).

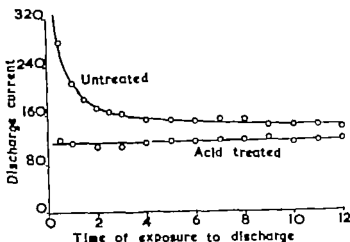


Fig 4

Variation of the Discharge Current with Time f Exposure to Dis harge i A idtreated and U treated Dis harge tubes.

Like data were obtained in bromine vapour The current ttained saturation within an ppreciably short time interval Thus for water vapour the current reach d the minimum stationary val within 10–12 mins, while for iodi e and bromine within 4–6 min The minimum saturation value of *i* for a fixed electrode separation and gas pressure appeared to be the same whatever may be the predischarge interval (Curves 1–4 Fig. 3) The results in Fig. 4 further show that the above time variation of the discharge current is markedly affected by acid treatment. In acid treated ozonisers the conductivity rem ined unaltered within experimental accuracy (*cf* Curves 1 and ‥ Fig 4)

DISCUSSION

The following are the imfortant conclusions from the foregoing results :—

(1) The conductivity of a gas introduced into a degassed vessel decreases markedly to a minimum value characteristic of the system and pressure.

(2) The time-rate of decrease of is exceedingly rapid.

(3) The results are markedly affected by acid treatment.

It has been reported in the previous communication [47] that the (instantaneous) current in a discharge is giv n by

$$= i_0 \frac{(\alpha-\beta)\ e^{(\alpha-\beta)\ x}}{\alpha-\beta\ e^{(\ -\beta)\ x}} \qquad \text{(i)}$$

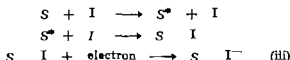
Here $_0 = n_0\ e$ where n_0 is the number of primary electrons, of charge e to be released from the cathode surface and responsible for the production of electron avalanches The Townsend first coefficient α depends upon the position x in the nonuniform field Further when is much grater than the second coefficient β the equation (i) is written as

$$i = {}_0 \frac{\alpha\ e^{\int\ d\ x}}{\alpha-\beta\ e^{\int \alpha d\ x}} \qquad \text{(ii)}$$

From this, it is clear that the current and the creation of electron avalanches are fundamentally governed by n_0, α and β The Townsend coefficients α and β depend upon the applied field and gas pressure For a fixed potential fed to the discharge tube of known dimensions, the field under the experimental conditions is constant. The gas pressure was observed[38] to decrease with time of exposure to discharge This aspect was well investigated in hydrogen by Johnson,[32] the pressure of hydrogen as measured by a micromanometer constructed specially for the purpose remained sensibly constant when the system was kept unexcited when the fields were applied, the hydrogen content decreased rapidly to a minimum value. The decrease was of the order of 0 03–0 04 mm Hg The theoritical considerations on electrical discharge in gases suggest that a reduction in gas pressure increases the current,

as actually observed [14] The result (i) reported above in this paper the decrease of the conductivity was ttributed to the reduction of the primary electrons on account of progressive sorption of gases under discharge This is in accord with the observation that photo and thermo-electric currents decreased with th adsorption of electronegative atoms (or molecules) These last on account of their electron affinity capture electrons and thus retard their escape from the surface [15]

Th above consideration suggests that if S represents a Langmuir site on clean glass surface sorption of iodine atom thereon and the subsequent capt re of electron can be represented as



$$S + I \longrightarrow S^{*} + I$$
$$S^{*} + I \longrightarrow S \quad I$$
$$S \quad I + \text{electron} \longrightarrow S \quad I^{-} \qquad \text{(iii)}$$

This formulation would emphasise that atoms adsorbed on glass retain their electro-negative character This however invalidates the current view that atoms are held by Langmuir adsorption on glass by having an lectron from alkali atom in glass

The rate f current decrease gives a striking support for the above vi w that the adsorbed gas is responsible for the finding (i). It is exceedingly rapid and ttained saturation within 5–12 mins Essentially similar result *viz.* rapid te of sorption unde discharge was recorded by a number of investigators. Employing spectroscopic methods Taylor observed that the disappearance of hydrogen in hydrogen–neon tubes was accomplished within 5 mins As mentioned above Johnson[17] tudied th sorption of hydrogen under electrodeless discharge nd t nd that the saturation in the pressure–decrease attained within 4 mins Willows and George[14] investigated sorption under discharge of various gases and noticed that it was complet in 5–8 mins

Further Bangham[19] has sh wn th t the rate of sorption f a gas on glass is well represented by th f llowing relationship

$$S = k\, t^{1/m} \qquad \dots \qquad \text{(iv)}$$

where S is the mount adsorbed upto time t m and k re constants. This equation was found to be applicabl in a number of systems[20,] not only with glass as an adsorbent but also with a

variety of crystalline and semi-crystalline solids e. g taking up of iodine by charcoal[28] sulphurdioxide and ammonia by sodium chloride and saphire [14] ammonia by carborundum powder[30] and oxygen by activated graphite [14]

From the above argument if we make an assumption that the decrease (δ) of the current upto time t is due to the amount of gas adsorbed one would expect that

$$(\delta_1) = k \quad t^{1/m} \qquad \text{(v)}$$

It follows therefore that

$$\log (\delta_1) = \log k + 1/m \log t \qquad \text{(vi)}$$

It is instructive to see from Fig 5 that log (δ) varies sensibly linearly with log t as required by the equation (vi)

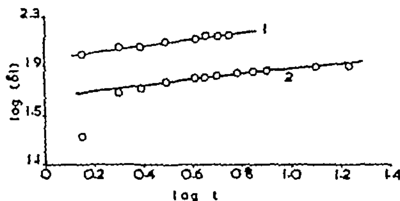


Fig 5

V riation of log (δ) with log t in iodine vapou (urve 1) and water vapou (urv 2)

It may be mention d that washing the discharge tubes with acid solutions altered markedly the above data. Similar results were obtained in Joshi effect (Δ). While in untreated ozonisers the effect could be observed immediately in acid treated vessels a certain amount of ageing was found necessary to initiate Δi [31] This disparity was attributed to the presence of alkali on the surface of former type of ozonisers which enhanced sorption to aid the occurrence of Joshi effect. Even in the measurements of sorption of gases the presence of alkali on glass surface played an important role [32] Faraday[33] observed large adsorption of water

vapour on glass and attributed it to the existence of alkali when this last was removed by washing glass surface with acids no appreciable sorption was noticed Similar data was recorded by Warburg and Imhori[86] and Harries and Schumacher[87] This catalytic activity is however a general feature of such polar substances knowledge of a number of reactions which are controled by the presence of traces of some polar substance is available [88] Norrish[89] has emphasised that the enhanced activity of gas reactions in the presence of small quantities of NaOH KCl etc is due to the distortion on account of the strong local disturbing forces available at the surface of the polar substance in the stable configuration of the molecule such that these last become more vulnerable to be attacked. Lennard-Jones and Dent[90] envisaged the various forces existing outside the surface of the polar substance :—*(a)* direct electrostatic force between ions in the solid and in the free state outside it *(b)* forces of attraction due to induced dipole in the centre of an atom or ion and the electrostatic field *( )* forces due to polarisation in the substance by the free charges outside ; and *(d)* van der Waal's forces. Of these, van der Waal's forces play a primary role they act as the first agents in the process of adsorption of atom or ion and the electrostatic forces serve to clinch the capture of ultimate adsorption.

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5

STUDIES OF JOSHI EFFECT AND SECONDAPY EMISSION IN A LOW FREQUENCY ELECTRODELESS DISCHARGE*

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{Abstract: Cathode ray oscillographic studies of a low frequency electrodeless discharge in iod ne vapour showed the existence of d fferent types of pulses of these the longer ones ( ) produced by the secondary electrons released from the cathode were inhibited, while the shorter pulses ( ) due to photoionisation of the gas particles in the cathode fall region were favoured by external light and applied fields At larger values of these last another kind of pulses ( ) unrelated to (or ( ) were noticed their origin appeared unknown While the number of ( ) was unaffected that of ( ) was decreased by magnetic fields.

The data gave an experimental evidence for the inhibition under light of the secondary emission from the cathode further unlike in d. c discharges photoion sation in the gas phase appeared significant for the maintenance of the discharge now investigated.}

INTRODUCTION

1 Professor Joshi s discovery of the photovariation (i) $^{1}\Delta i^{2}$ usually though not invariably dim nution of the discharge conductivity and the number of the associated pulses observed on a cathode ray oscillograph opens a new field of research on electrical discharge in gases. The significance of the secondary

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The work reported here w rried ou in the Chemical Laboratories Be ara Hindu U iversity Be ras.

emission in the maintenance of a discharge *(vide infra)* has been emphasised,[3,4] It was of interest therefore to investigate the effect Δi and other factors mentioned later The present commu nication reports the details of a few studies made by us from this point of view in a low frequency lectrodeless discharge in iodine vapour

THEORY: A BRIEF OUTLINE OF THE PROCESSES IN ELECTRICAL DISCHARGE

2. In the begining we propose to give a brief resume of the various processes occuring in electrical discharge in gases It is felt that this will be not only of a help to future workers in this field, but also eliminates discrepancies in employing a few symbols The method usually followed by Professor Lenard B Loeb under whose able guidance this complicated subject has advanced to a very large extent, has been adopted.

Ordinarily there exists in gases an exceedingly small number of electrons produced by ionising effects of radioactive and cosmic rays. When large fields are applied to the electrodes separated by a gas, these free electrons acquire energy and ionise atoms or molecules by inelastic collisions ionisation by electron impact i the chief feature of electrical discharge (Townsend) The resulting electrons in their turn repeat th process to yi ld electron avalanches which are primary for determining the electrical conductivity in a discharge[4] The magnitud of the current is controlled by the number of avalanches produced in unit time

Depending upon the origin of carriers of electricity electrical discharge in gases m y be divided in to two classes[4] nonself maintained and selfmaintained disch rge In th form the *primary* electrons responsible for the production of electron avalanches, are generated by som external agencies like radioactiv or light rays. The discharge exists so long as these last are in operation. This may be illustrated by the circumstance invol ed in the Geiger region of the counters. The potential applied between the wire and the ylinder of the counters is but sufficient to energise electrons to cause ionisation by collision this will happen only when once an electron is introduced into the system by external agencies In a selfmaintained discharge "the gas

intensified photo-electric or ionisation current develops a mechanism by which new electrons can be generated in sufficient number by secondary processes in a sensitive portion of the discharge to replace externally imposed ionisation"[4] That is in the case of a selfmaintained discharge the agencies developed in the discharge space e g. photons, positive ions etc produce electrons which in turn cause avalanches and their generators, a cyclic operation takes place This will happen when the externally applied voltage is larger than a minimum value we can roughly take this value as the threshold potential V_m which is in use for long time in this field of research and the significance of which for the discharge reactions in general and for the effect Δ in particular has been emphasised.[7] The threshold potential V_m is the *starting potential of a selfmaintained* discharge

The various secondary processes active for the selfmaintained discharge are as follows —

A In the gas phase —

(i) ionisation and excitation by electron impact
(ii) ionisation by positive ion impact,
(iii) photo-electric action in the gas, and
(iv) action of metastables in the gas

B. At the cathode —

(i) electron bombardment
(ii) positive ionic bombardment
(iii) photo-electric effects
(iv) impact of metastable atoms and
(v) field currents

The first process (A i) is generally referred to as Townsend's a mechanism is defined as the number of electrons created by ionisation of gas particles by electron impact per cm advance in the field direction by a single electron. This is the only process occurring in the Geiger or nonselfmaintained region *(vide supra)* The current due to this process is given by

$$i = I \; e^{ax} \qquad (1)$$

Here $I = n_o e$ where n_o is the number of primary electrons of charge e and x the electrode separation.

The significance of the other processes for the selfmaintained discharge has been emphasised by Loeb[4] of these liberation of electrons from the cathode by positive ionic bombardment (BII) referred to γ mechanism and by photons created in the gas (BIII) mentioned as $\eta \theta g$ process (θ is the number of photons produced in the gas by an electron in advancing on cm path in the field direction g is a constant representing the fraction of photons that can reach the cathode and η is the fraction of photons which produce electrons that succeed in leaving the cathode) are important. The w ll known β processes refer to any one or more of the allowed secondary processes (AII–Bv) while γ and $\eta \theta g$ indicate these last mentioned specific mechanisms (BII and BIII). The Townsend coefficient β is defined as the number of new electrons created by a positive ion during its m vement per cm path in the field direction by ionization of neutral ga particles[•] The instantaneous current in a discharge is roughly given by

$$= i_o \frac{(-\beta) \quad e^{(-\beta)\, x}}{a - \beta \quad e^{(-\beta)\, x}} \qquad (2)$$

$$i = i_o \frac{e^{\;x}}{1 - \gamma\left(e^{ax} - 1\right)} \qquad (3)$$

or $$i = i_o \frac{a^{\;ax}}{- \eta \theta g\left(e^{(\;\;\mu x)} - 1\right)} \qquad (4)$$

In (4) μ is the bsorption coefficient of ph ton in the gas. For the details f these equations and especially for their altered nature in nonuniform fields, the read is referred to th uthoritative treatise Fundamental processes in lectrical discharge in gases by Loeb

The above characteristics are roughly true for discharge with alternating fields, especially when the conditions are not complicated by accumulation of space charges the processes under these circumstances are by no means fully understood.

It may be mentioned that in recent communication Dr Arsiker[•] represents the liberation of electrons from the cathode by photons as γ–mechanism and by positive ions as β–mechanism; this is however different from the usual method f representation.

It may be pointed out that in discharge with solid dielectric electrodes like glass the contribution of secondary electrons from the cathode material is, however limited or little since unlike in a metal the *free* electrons referred to as Fermi gas are negligible in glass Electron emission from glass is improbable. It is therefore, assumed that the electrons deposited on the glass walls in the preceding half cycle and remaining unneutralised on account of their dielectric nature constitute the secondary emission, this point has been well developed by Professor Jatar[19] of Saugor University

EXPERIMENTAL

§ 3. In the present investigation cylindrical glass tubes with closed ends were employed (Fig 1) they were filled with iodine vapour at a desired pressure They were excited by external sleeve electrodes (S_1 and S_2) or metallic disc electrodes (T_1 and T_2, Fig 1) fixed externally at the ends of the tubes, alternating potential (0. 5 to 8kV) of 50 cycles/sec were used. The current structure was investigated by a cathode ray oscillograph (C. R. O). For this purpose a noninductive noncapacitative carbon resistance R was introduced in the circuit and the potential developed across R was fed to the deflecting plates of the oscillograph (Fig. 1).

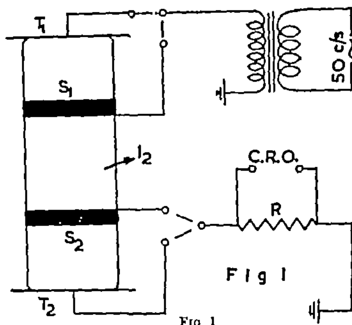


FIG 1

Experimental set up f the oscillographic studies of l w frequen y lectrodeless dis h rge in iodine vapou

RESULTS AND DISCUSSION

§ 4. 1 *Nature f the Pulses.* Fig 2 gives a typical series of oscillograms representing the current structure of a low frequency lectrodeless discharge in iodine vapour (p=0 47 mm Hg) at varied applied potentials It was observed that on every half cycle of the current trace were produced some transient pulses. By suitable

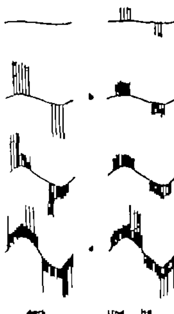


Fig 2

Oscillograms representing the current structure in l w frequen y electrodeless discharge in iodine vapour in dark and under light at ( ) 1.8, (b) 1 9, ( ) 2 8 and (d) 7.5 k (50 cy les/sec).

adjustment of the controls of th o r o that is, by increasing the sweep frequency th nature of a single pulse could be studied. It appeared generally *(vid infra)* as a critically damped wave (cf. Fig 3a) composed of two phases, one representing a very steep rise and the other a slow process of decay of the curve The pulse is defined by Korff[11] as the potential drop of the anode It has been mentioned that under fields the electrons acquire energy and ionise gas particles and yield avalanches. The produced electrons deposit themselves on the anode in an appreciably short time interval on account of this, the corresponding potential decreases and this

reduction is manifested in the form of the steep rise of the current trace of a pulse The latter part of the curve represents the recovery of the anode potentials to its narmal value this is however comparatively a slow process; it is due to the deposition of *slow* moving positive ions produced in the avalanche formation on the cathode It was estimated that the total pulse tim was approximately 2x10– sec [11] As pointed out earlier [8] the (repeti tion) frequency of the pulses observed on a c r o. corresponds roughly to th t of th Trichel pulses (of the order of a few kc/sec) detected in a negative corona

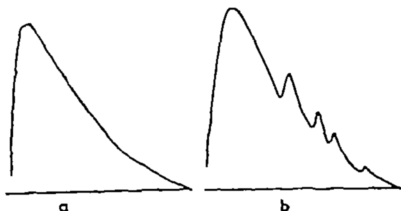


Fig 3

N ture of pulse t different i ter-el trode separations (x) (a) 18 mm and (b) 90 mm.

When the electrode separation (x) was large the wave form especially in th later phase of the pulse was found to be of demped nature (Fig. 3b) This irregular behaviour of the declining part of the current trace of a pulse chiefly at large x would suggest that it may be connected with the positive ion accumulation or space charge shown by calculations to be possible even with low frequency potentials at enhanced electrode separations like 9 cm.

4 2. *Types f Pulses and their Origin.* A study of the oscillograms in Fig 2 indicates that under ordinary conditions *(vide fra)* there occurred chiefly two types of pulses–(i) the longer pulses and (ii) shorter pulses From the definition of a pulse it follows that the larger the potential drop the longer is the pulse height. The longer pulses (i) were therefore attributed to

enhanced number of avalanches created by fast moving electrons released from the cathode by γ and $\eta\theta_g$ processes (of § 2) while the shorter pulses (ii) were produced by avalanches generated by electrons formed in the gas phase by other secondary processes (β) Invariably pulses of large amplitude occurred in the beginning of the current trace and then the shorter ones follow; it seems therefore that when the alternating potential exceeds the breakdown value of the medium the γ and $\eta\theta_g$ mechanisms take a significant part in the initiation of a discharge and lead to the production of favourable circumstances for th development of other secondary processes. For example the photons produced in the course of the formation of avalanches leading to (), may be bsorbed by the gas particles to regenerate electrons which give rise to (ii) As will be shown later photoionisation in the gas phase appears primary to the shorter pulses (ii)

§4. 3 *I fl ence of Appl ed potential on the prod iction of Pulses.* The oscillograms in Fig 2 further point out the marked dependence of the production of the pulses on the applied potential V When this last was not sufficient enough to cause a selfmaintained discharge i. e. at $V < V_m$, the current trace under simple enough conditions sy in the absence of external light, was but sinusoidal without any superimposition of any pulses When V was just equal to V_m, remarkably enough the longer pulses only were observed in every half cycle these were roughly of equal height indicating that the number of avalanches necessary to constitute a pulse was sensibly the same for every pulse Increase of V decreased the number of (i) and initiated the shorter pulses which occurred always after one or a group of longer pulses *(vide supra)* Further th shorter pulses also were roughly of the sam amplitude Electrons created by th photoionisation of a gas particle chiefly in the neighbourhood of the cathode acquire energy under fields and start ionisation by inelastic collisions with atoms and molecules approximately from a fixed point away from the cathode (Fig 4) The generation of electrons increases however initially exponentially and decreases as they recede from the cathode to weaker fields. The ion production continues until the field becomes too weak to cause ionisation by collision. The region between this point (say , see Fig 4) and the earlier one ( ) from which ionisation by electron impact predominates, may be referred to roughly as the plasma region of the discharge under investigation

It may be mentioned that ionisation of the gas particles between cathode and the point r is not excluded and occurs by the rapidly moving electrons released from the cathode by γ and $\eta\theta g$ processes (Fig. 4).

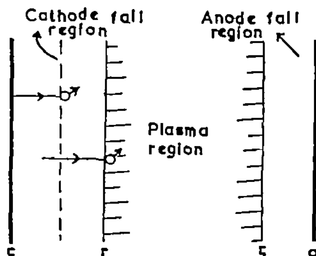


FIG 4

Plasma region in l w frequen y electrodeless dis harge.

At much large γ the production of the longer pulses was inhibited appreciably only one pulse of this type could be detected at the beginning of that phase of the alternating cycle at which and above the voltage was enough to cause ionisation by collision This pulse persisted over a wide range of γ Under these condi tions the current trace was superimposed over an appreciable part of it by th pulses of type (ii) It appeared that the discharge t these potentials was completely maintained by the processes responsible for (ii). This observation led us to suggest[11] th t photoionisation in the gas phase was a significant secondary mechanism for the maintenance of a low frequency electrodeless discharge in iodine vapour It may be mentioned that this feature brings out a distinction between low frequency discharge and that with d c. potentials, since in this last case it has been emphasised that the above mentioned process is insignificant especially in a nonheterogeneous gas

The inhibitive effect of large fields on the production of larger pulses, was remarkable Other workers[1] appeared to have noticed essentially similar results in chlorine no distinction regarding the different types of pulses as that pointed out in the present paper could however be mentioned. Presumably a marked difference in the heights of pulses (i) and (ii) might not have existed under their experimental conditions this circ mstance will definitely occur under conditions favouring large ionisation zones or wide plasma regions; at a suggestion due to present senior author one of us (M G B) has investigated this factor and the details will be gi en elsewhere[14] The inhibition of the pulses with enhanced V it w s argued, was not due to the photons created in the course of time in which the previous pulse occurred. It follows from that at large V increased ioni bombardment on the electrode surface causes dissociation of adsorbed molecules to yield atoms or/and radicals with large electron affinity these capture the secondary electrons (contributed by electrons deposited in the preceding half cycle and remaining unneutralised on account of th dielectric property of the glass walls, vide § 2) to be released from th cathode by γ and $\eta\,\delta g$ processes and responsible for (i). In gases containing metastables e g. in chlorine th same vis. th dissociation of surface adsorbed molecules to inhibit the secondary emission, can happen with the high energitic and long life-particles[11]

It may be pointed out that t V V_m altogether different kind of pulses (iii) have been noticed. These occurred chiefly t th end of the half cycle and had roughly the same height as th pulses of type (i) (Fig. 2d). While the pulses (i) or (ii) ppeared on the current traces regularly one after nother these new pulses found their place intermingled with (ii) with no sequence whatsoever Th p lses (i) or (ii) were ffected by external radiation *(vide infra)* whereas this last appeared to have no infl ence on the pulses of type (iii) detected in iodine vapour The origin of these pulses howeve needs further investigation.

4.4 *Influence of Irradiation Joshi effect* The data in Fig. . further show the effect of exposure of the discharge tube to th light from a 200 watt (glass) bulb At potentials V below V_m especially in the nonselfmaintained region of th discharge irradiation initiated the shorter pulses (Fig 2a) this was mentioned a positive Joshi effect $+\Delta i$ At $V = V_m$ external light inhibited

markedly the observed longer pulses (Fig. 2b) to give the negative Joshi effect, $-\Delta$ this last attained invariably its maximum at this potential V_m. Remarkably enough the decrease in the number of the longer pulses under light was accompanied by the simultaneous production of shorter pulses (Fig 2) this indicates the co-occurrence of positive and negative effects, $\pm\Delta i$ anticipated from altogether different studies with the observations of the rms val e of the current and its variation with the determinants like external light, its intensity and frequency and the resistance and capacitance of the measuring circuit, etc At potentials above V_m the oscillograms under light contained only the pulses (ii) which were of the same height, characteristic of the Geiger or nonselfmaintained region of the discharge in which Townsed α-mechanism only was operative but the externally impressed voltage was known to be enough to maintain the secordary processes also. This indicated that light inhibited these last especially from th cathode as illustrated by the preferential inhibition under light of longer pulses which were produced by γ $\eta\,\theta$ g mechanisms It may be pointed out that at $V \gg V_m$ (Fig 2d) the one longer pulse which occurred just at the beginning of the ionising phase of the alternating cycle could only be suppressed This observation would strikingly support the above mentioned inhibitive action of light on pulses (i). Further irradiation initiated or/and increased the number of shorter pulses these were of the same properties as those produced at $V > V_m$, in the absence of external light. The favourable influence of irradiation on the occ rrence of shorter pulses suggested that of the various processes (secondary) occurring in the gas phase and responsible for (ii) photoionisation in the gaseous medium was fundamental to their production.[1] It may be argued on similar grounds that of the two processes viz., γ and $\eta\,\theta$ g, responsible for (i) positive ionic bombardment on the catode (γ) is primary to the longer pulses however the evidence is inadequate to confirm this deduction

For the occurrence of the effect Δi Professor Joshi[10] suggests that *(a) under discharge an adsorption-like layer consisting of* excited particles, ions and electrons, and characterised by a low work function is formed *(b)* electrons are emitted under light from this boundary l yer *(c)* negative ion formation due to capture of these photoelectrons by excited neutral particles, especially atoms or/and radicals with large electron affinity causes

a current decrease as a space charge effect and (d) uncaptured electrons and their secondaries give the positive ffect $+\Delta i$ Th observed photo-increase ($+\Delta i$) of the rms value of the current and the initiation under light of pulses at potentials $V < V_m$ wa reported to be in striking agreement with th postulates (b) nd (d) Capture of electrons is possible only when their velocity is low when this last increases, the probability of their being captured decreases, *i. e.* the population of uncaptured electrons increases. From the considerations put forward in this communi cation electrons released from the cathode by any mechanism and unhindered by subsidiary processes especially on account of their large velocity should lead to the production of longer pulses, but not the shorter pulses as observed (Fig 2). Further at constant light frequency increase of applied V from values below threshold potential to those above V_m will cause the velocity of photo-electron larger and larger this should reduce the probability of lectron capture and lead to larger positive Joshi effect $+\Delta i$ at $V > V_m$ than that observed at $V < V_m$ how ver t $V > V_m$ appreciable negative effect is observed

Harries and E gel[13] and one of us[14] (N A R.) suggested simultaneously that light augments the dissociation of molecules held by van der Waal s forces on a primary Langmuir layer on the electrodes, to yield atoms or/and radicals which red ce the secondary emission to give th negative Joshi effect $-\Delta i$ The positive effect $+\Delta i$ is du to photoionisation of pre-excited particles on or/and in the vicinity of the cathode[11] The suppression of the longer pulses and the creation of shorter pulses under light follows from this hypothesis. There are h wever a few experimental findings, unconnected with the present studies, which cannot be explained by this mechanism also. The limitations of not only these two suggestions, but of all surface layer theories f the phenomenon are discussed elsewhere[11]

4.5 *Influence of External Magnet c Field* Oscillograms obtained when the discharge tube was subjected to a transverse magnetic field H were returned in Fig. 5 It was interesting to note that H ($\sim$400 gauss) decreased the number of the shorter pulses only H had no effect on the longer pulses. The following will help to account for these observation Fig. 6 represents a rough picture of the processes occurring in one half cycle t

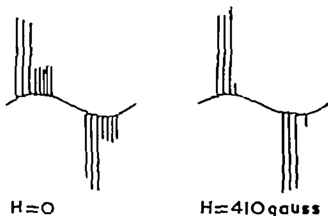


Fig 5

Oscillograms representing the tion of external magnetic field on the pulses f low frequency electrodeless discharge.

a plane cathode and anode in a magnetic field. The considerations mentioned below will pply only to circumstances where there is no accumulation of (positive ionic) space charges in which case the conditions are highly complicated. Calculations showed that with low electrode separations (X=20mm) and low frequency (50 cycles/sec) potentials the positive ion accumulation is little It is not necessary to state that in the abscence of magnetic field the path of the electron is in the fi ld direction. Under otherwise conditions the path is determined by the electric and magnetic fields electrons in a unifrom H move in circular paths whose (Larmour) radiu R is given by the well known equation R=m v/H e where m/e is the ratio of the mass to charge of an electron and v its velocity determined by the field.[14] In Fig. 6, A at the cathode f ll region represents the trajectory of an electron making no collision with gas particles. It d electron in the abscence of H will enter to the production of electron ar deflects this electron way from leads to a loss in the generation however cannot have any i region since the corre effect on the fast to γ and η proc

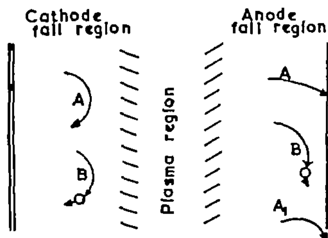


FIG 6

Effect f m gnetl field on electron trajectories t the cathode and anode.

on the longer pulses *(vid supra)* In Fig 6 B refers to the trajectory of an electron causing an inelastic collision with a gas particle as it is d flected away from the ionisation zone the resulting lectron possesses very little initial velocity nd its path will lso be cycloidal At the anode (cf. Fig 6) the d flected trajectories of electrons making collisions (B) or no collision (A) with atoms do not lead to appreciable loss in ion collection at the anode when electrons are removed out of the discharge space due to (H) (of trajectory A) it how ver leads to a decrease in the number of ions to be collected at the anode This is referred to the enhancement of diffusion coeffi ient under H which causes to a reduction of the verage pulse height but not the inhibition of a complete pulse The loss of an lectron in the cathode fall region causes a red ction in th valan he production, while that in the *anode fall region leads to decrease in the collection of a few ions* at the node. The observed inhibition under H of pulses of type (ii) appears therefore to be due to the former reason From the studies of the rms values of i and the variation thereof under H it has been deduced in a recent communication that the changes occurring in the anode fall region are significant the present oscillographic data are however indicative of a contrary conclusion.

ACKNOWLEDGEMENTS

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6

COMPARATIVE INVESTIGATIONS ON THE COLLOIDAL BEHAVIOUR OF PRUSSIAN AND TURNBULL S BLUES AND THEIR COMPOSITION

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[Abstract: In this paper the effect of uni bi, te and tetravalent ions on the coagulation of Prussian and Turnbull s blue sols has been studied under vary ng conditions of concentration, dilution purity and age of the sols. The sols behave normally with various electrolytes on dialysis dilution and ageing The abnormal dilution effect with monovalent electrolytes has been explained on the basis of ionic antagonism The coagulation values of electrolytes in the case of aged samples of turnbull s blue and prussian blue of the same concentration have been found to be almost identical and from this an evidence has been gathered in regard to the identity of the composition of both th blues as had been observed by Hofmann (Ann len, 1904 1 36) Muller (J prakt Chem 1922, 104 2410) by nalytical methods and by Saxena and Bhattacharya (J I C. S 1951, 28, 141 149- 221 224 703 709- 1952 29 529 534) by physico-chemical studies.

Although sulphide and hydroxide sols have been investigated more frequently and elaborately by many workers Schulze (J practishe Chem 25 431 1882) Hardy Zeitsch, physik, Chem 33 385 1900), H. Freundlich (Z, physik Chem, 44 129 1903 73 385 1910) Ostwald (Kolloid, Z 1920 26 69) and Ghosh and Dhar (J Physical Chem, 1927 31 187) the references to the investigations on the behaviour of more complex sols have been comparatively rare No systematic study has so far been made on the colloidal properties of turnbull s blue A fairly extensive work has been done on the coagulative properties of prussian blue sols but it is rather interesting to note that there exists a fundamental

difference as well in the experimental results obtained by recent workers 'Weiser Ghosh and Dhar' The colloidal studies of these blues prepared under similar conditions may also throw some light on the identity of their composition In view of this, it was thought necessary to carry out as far as possible comparative investigations on the coagulating properties of these sols The previous investiga tions so far made on prussian blue sols were in presence of oxalic acid used as the peptising agent which might vitiate the inferences and hence I have studied the colloidal behaviour of prussian blue prepared by adding excess of $K_4Fe(CN)_6$ only which acted as a stabilising agent.]

EXPERIMENTAL

Prussian blue sol (A of concentration 2 gms./litre) was prepared by mixing 1 equivalent of $FeCl_3$ to 5/4 equivalents of $K_4Fe(CN)_6$ *i. e.*, 12.4c.c. of N/2.664 FeCl and 8.5c.c of N/1.952 $K_4Fe(CN)_6$ and the soln. made upto 500c.c.) Turnbull's blu sol of the same concentration prepared by mixing 1 equivalent of *ferrous sulfate and 5/4 equivalents of $K_3Fe(CN)_6$ was found to be* unstable and hence a more stable sol was prepared by mixing th reactants in the ratio of 1 : 3/2 *i. e.*, 10.4c.c of N/2. 06 K_3F $(CN)_6$ added to 5.06c.c. of N/10 FeSO 7H_2O and the soln. made upto half a litre.)

The coagulation of the sol was studied as described by H. Freundlich (*Colloid* and capillary chemistry) *5c.c of the sol was* taken in test tubes, varying amount of electrolytes were then added and the soln. made upto 10c.c in each case by th addition of water The mixture was thoroughly mi ed and the test tubes were left in the rack for one hour The vol. of the lectrolyte which just coagulated the sol in one hour is noted from which th precipitation concentration is calculated.

The coagulation values of various electrolytes have been determined for undialysed dialysed and aged samples of prussian and turnbull's blue sols at various dilutions

Table I

Undialysed prussian blue sol of concentration 2 gms./lit is denoted by A

Coagul ting lectrolytes	PRECIPITATION CONCENTRATION		
	A = 2 gms./lit	A/2 = 1 gm./lit.	A/4 = .5gm /lit
LiCl	1 15M/lit.	1 01 M/lit	0 98 M/lit
KCl	17	19 „	.52 „ „
NaCl	1 05 „	.58 „ „	·215 „
$BaCl_2$	0065	0060 „	0035 „
$CaCl_2$	00299 „	008 „	007 „
$MgCl_2$	0336 „	·029	027
$ZnCl_2$	0008	0005 „	0005 „
$CdCl_2$	001 „	00058 „	00055
$CrCl_3$	00042 „	00021 „	00016 „
$AlCl_3$	00073 „	00043 „	00°8 „
$Th(NO_3)_4$	00031	00018 „	·000137 „
$Ce(SO\ )_3$	00047 „	·0004	00037 „

Table II

Prussian blue sol A of concentration 2 gms./lit dialysed for 3 6 and 9 days.

Coagulating electrolytes	PRECIPITATION CONCENTRATIONS Period Dialysis		
	3 day	6 days	9 day
LiCl	.82 M/lit.	688 M/lit	.58 M/lit
KCl	135	137	115
NaCl	66	.56	40
$BaCl_2$	0015	000825	0006
$CaCl_2$	004‿5	00385	00177
$ZnCl_2$	0006	00046	00043
$MgCl_2$	011	00725	0065
$CdCl_2$	00064	00060	00057
$CrCl_3$	00026	00019	00014
$AlCl_3$	00032	00024	00021
$Th(NO_3)$	00024	00018	.000137
$Ce(SO\ )_3$	00042	00029	00024

Table III

Aged Prussian blue sol A=2 gms./lit, period of ageing 25 days coagulation values of electrolytes on diluting the sol to A/2 and A/4

Coagulating electrolytes	PRECIPITATION CONCENTRATION		
	A=2 gm /lit	A/2=1 gm./lit	A/4= 5gm /lit
LiCl	1 1 M/lit	96 M/lit	.88 M/lit
NaCl	98	.54	47
KCl	155	17	19
$BaCl_2$	0055	00475	004
$CaCl_2$	0259	008	0065
$MgCl_2$	022	028	023
$ZnCl_2$	00065	0005	0004
$CdCl_2$	0007	000502	00041
$CrCl_3$	00026	00033	00012
$AlCl_3$	.00066	00028	00022
$Th(NO_3)_4$	00029	000162	00012
$Co(SO\ )_3$	.00045	00036	000337

Table IV

Undialysed Turnbull's blue sol A=2 gms./lit, prepared by mixing 1 equivalent of FeSo and 3/2 equivalents of $K_3Fe\ (CN)_6$

LiCl	1 18 M/lit	1 15 M/lit	1 06 M/lit
NaCl	1.115	1 07	60
KCl	14	17	19
$BaCl_2$	.012	0076	0055
$CaCl_2$	021	027	019
$CdCl_2$	00115	.00059	00040
$ZnCl_2$	0041	00055	00025
$MgCl_2$	.034	0303	025
$AlCl_3$	.0012	.00063	00026
$Th(NO_3)$	00041	00022	00015
$Co(SO\ )_3$	.0006	.00047	00025

Table V

Turnbull's blue sol of concentration 2 gms /lit. dialysed for 3 6 and 9 days

Coagulating electrolytes	PRECIPITATION CONCENTRATION Period of Dialysis		
	3 d y	6 days	9 days
LiCl	68 M/lit	.59 M/lit	.54 M/lit
NaCl	.54	.52	.50
KCl	13	12	115
$BaCl_2$	00105	0009	0007
$CaCl_2$	00425	004	00345
$MgCl_2$	0105	0091	0075
$CdCl_2$	.000557	000545	000516
$ZnCl_2$	00052	0005	00046
$CrCl_3$	000258	000208	00019
$AlCl_3$	000333	0003	00028
$Th(NO_3)$	00019	00016	00014
$Ce(SO_4)_2$	00039	00024	000?0

Table VI

Aged Turnbull's blue sol A (undialysed) of concentration 2 gms /lit. period of ageing 35 days Coagulation values of electrolytes on diluting the aged sol A to A/2 and A/4

Coagul ti g lect olytes	PRECIPITATION CONCENTRATION		
	A = 2 gms /lit	A/2 = 1 gm /l t	A/4 = .5 gms./lit
LiCl	1 06 M lit	80 M/lit	68 M/lit
NaCl	06	.80	.56
KCl	13	14	155
$BaCl_2$	0115	006	0035
$CaCl_2$	.0268	021	013
$MgCl_2$	031	028	0206
$CdCl_2$	00065	0003	00016
$ZnCl_2$	0005	00025	000137
$AlCl_3$	00096	0003	00015
$CrCl_3$	00035	00019	00012
$Th(NO_3)_4$	00036	00016	0001
$Ce(SO_4)_2$	0005	00035	00023

DISCUSSION

It has been observed th t the Schulze-Hardy law is followed in the general sense that the greater the valency of the oppositely charged ion the greater its coagulating power in other words, the coagulating powers of Th Ce >Al‴ Cr‴ >Ba Ca Mg″,Zn Cd >K ,Na ,Li

From the observations recorded in table II V it is evident that the behaviour of both the blue sols is quite normal towards electrolytes on progressive dialysis. The investigations throw further light on the relationship between the influence of dialysis and the stability of the sols. The stability decreases with the number of days th sol has been dialysed in other words, as the purity of the sol increases.

With monovalent electrolytes, the coagulation values gradually *decrease with dialysis* Th *general* behaviour of bivalent electrolytes,Zn and Cd regarding the gradual fall of precipitation concentration with purity of the sol is similar This is in conformity with the electrochemical behaviour of zinc and cadmium their precipitation values are also very close to each other The fall in concentration of Ba Ca Mg with progressive dialysis seems to be similar although there exists much difference between the precipitation concentrations taken individually The trivalent ions Al‴ Cr‴ have got much less precipitation concentration while tetravalent ions Th‴ Ce‴ have the least ppt concentrations.

On dilution, the concentration of the sols decreases, consequently th ppt concentrations of all other lectrolytes also decrease except that of KCl which is found to increase.

The fundamental factors which play an important role in th coagulation of coll ids in general are (1) charge of the precipitating ion (2) adsorption of the stabilising ion. My results of quantitative estimations on adsorption of $K_4Fe(CN)_6$ by prussian blue and f $K_3Fe(CN)_6$ by turnull's blue have shown that prussian blue and turnbull's blue have fairly good capacity to adsorb ferro and ferri cyanogen ions respectively and further that the former had greater capacity of adsorption for ferrocyanogen ions than the latter had for ferricyanogen ions. My results of investigation are in full agreement with the views that the st bility of these sols is mainly due to the adsorption of ferro and ferri cyanogen ions respectively

because as the dialysis progresses, the stabilising ions are gradually removed with the result that the precipitation concentrations of the coagulating electrolytes gradually fall. That prussian blue has greater capacity to adsorb ferrocyanogen ions than turnbull's blue to adsorb ferricyanogen ions is further proved by the fact that with the progress of dialysis the stability of the turnbull's blue sol decreases much more rapidly than that of prussian blue *(vid tables 2,5)*

The abnormal dilution effect with monovalent electrolyte KCl has been explained by the ionic antagonism caused by the adsorption of ions bearing the same charge as the colloid particles Ghosh and Dhar (Jour Phys. Chem. 1927 31 647) have shown that the sol behaves normally towards dilution wh n the ions carrying the same charge as the colloid particles are not adsorbed in appreci able amount. Dhar and collaborators (J I C.S., 1929 6 644 1930 9 315· 1933 10 471) have studied th change of stability of various other sols like Ferric hydroxide Aluminium hydroxide and thorium hydroxide *containing appreciable amounts of stabilising electrolytes* and had drawn the same conclusions Although the dilution effect has been explained by *Ghosh* and *Dhar* as being due to the greater adsorption of stabilising ions, I am of opinion that the process is more complicated and is a result of consequitive or side processes such as (1) charge neutralisation (²) adsorption of stabilising ions (3) size of the particles (4) distance between the particles (5) the ph enomenon of hydrolysis which may also take place in some cases In coagulation processes therefore all these phenomenon are taking place simultaneously and are mostly responsible for th stability of a colloidal solution.

In the case of diluted sols the distance between the particles along with the adsorption phenomena and the concentration of the colloid seems to offer a more probable explanation for the abnormal behaviour with some monovalent electrolyte

The difference in the behaviour of these blue sols on ageing may be attributed to the difference in the size of the particles, other reasons such as charge hydration etc., may also prevail My observations on aged sols go to show that the precipitation concentrations fall on ageing. It appears that most probably the size of the particles increases on ageing and hence the decrease in the ppt. concentration is observed

My investigations on the colloidal blues throw further light on the existing views regarding th composition of soluble prussian nd turnbull s blues. In th light of my physico-chemical studies on their composition it may be concluded that the complexes of the types indicated are formed, indeed, but they undergo a change of state to that of a colloid by the adsorption of the stabilising ions. This view is further supported by the fact that on ageing the undialysed sols of prussian and turnb ll's bl es th y ppear to attain almost the same stage of dispersity The coagulating values of many lectrolytes (LiCl NaCl KCl $CaCl_2$, $HgCl_2$, $CdCl_2$, $Ce(SO_4)_2$ vide tables III, VI almost approach each other quantitatively both for undiluted and diluted aged sols. Regarding their composi tion also identity has been observed in the formation of the compound KFe [(Fe CN)$_6$] (vide publications J I. C S. 1951 141, 221 703 1952 529)

The foregoing observations regarding similarity of composition of prussian and turnbull s blue on ageing, are in agreement with the conclusions arrived at by Hofmann and Muller by analytical methods and by Bhattacharya by his studies on the absorption spectra and magnetic susceptibilities of these compounds (Zeit. anorg. Chem. 1933, 213 240 J I. C S., 1905 12 143, 1934, 11 325)

My grateful thanks are due to Dr A. K. Bhattacharya D.Sc of Agra College Agra, for his helpful guidance.

7

INFLUENCE OF AGING UNDEP ELECTRICAL DISCHARGE ON JOSHI EFFECT IN MERCURY VAPOUR

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INTRODUCTION

The occurrence of *Joshi-effect* detected first in chlorine[1] was found subsequently to be not a special feature of any particular gas or vapour but rather a general phenomenon since it has been observed in a number of systems,[2,3,4] *viz.*, oxygen nitrogen sodium potassium, bromine iodine and also in HCl, HBr and NO_2. Besides these homogeneous systems studies were made in certain mixtures of the above gases and vapours like air $Cl_2 + Br_2$, $Cl_2 + I_2$ etc. Recently these investigations were extended to mercury vapour[5] and remarkably enough 100 per cent relative *Joshi-effect* was observed under favourable conditions with but ordinary light The profound influence of 'aging' and wall effect emphasized by Prof Joshi soon after the discovery of the phenomenon and observed in the above-mentioned systems by him and his co-workers[6,7] was found in mercury vapour more pronounced than in any other excited medium. It was observed that, compared with other gases the production of *Joshi-effect* in mercury vapour necessitated the continuous 'aging under electrical discharge for unusually long periods. A systematic study in some detail of the above factor was therefore undertaken

DESCRIPTION OF APPARATUS AND METHOD

The behaviour of a number of ozonisers charged with mercury vapour (*vide infra*) was investigated The results now reported refer to two typical systems numbered 1 and 2. The former contained a globule of liquid mercury well outside the annular space

the seat of the discharge produced under the applied fields The discharge space contained therefore mercury vapour at a pressure of 0 002 mm Hg in equilibrium with the liquid phase The other ozoniser 2 contained only the vapour at the above pressure The dimensions of the ozonisers such as the l ngth and width of the annular space are 100 and 2 mm respectively for ozoniser 1 and 200 and 2 mm for 2 Arrangement was made to obtain a simultaneous and non-stop electric discharge in the annular spaces of the two ozonisers and it was conducted for about 440 hours. The electrical ircuit and the general set up are as follows Single phase A C of 50 cycle frequency was obtained from 220 volt mains and th potential was stepped up by means of a H. T transform r of ratio 20 000 150; The primary potential of th transformer was regulated with a potentiometric arrangement and the secondary potential was obtained from a knowledge of the transformer ratio and primary potential The low tension current was measured with a sensitive mirror galvanometer the detector being triode 30 coupled inductively with the low tension and used as a diode by short circuiting the grid and plate Current observations were mad when the ozonisers were in dark and irradiated with a 200 watt, 220 volt incandescent (glass) bulb at every 12 or 6 hours or even at smaller intervals of time as desired.

RESULTS AND DISCUSSION

The generality of these results is sufficiently represented by two typical groups of curves in Fig 1 which show the time variation

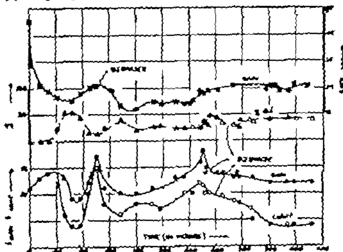


FIG. 1

of i (current in dark) i' (current in light) and $\% \Delta i = (\frac{i' - i}{i} \times 100)$. Only has been given in the case of ozoniser 2 since *Joshi-effect* $\Delta i = i' - i$ was not observed therein These curves show that despite the constancy of applied potential the conductivity was not constant but varied with duration of exposure of the system to electrical discharge until a long period of time Furthermore this time variation is characterised by discontinuities. The exciting potential was kept constant at 0.67 kV (r m. s) throughout the course of the experiment Its maxium fluctuation was less than 1/4th of 0.2 volt, which latter represented the least division on the scale of A C. volt-meter (Weston s) used. From the conductivity potential characteristics obtained for ozonisers 1 and 2, it was found that the current variations of the order of magnitude as shown by the curves of i with time at constant exciting potential corresponded to a potential difference of 0.2 to 0.5 of a volt in the primary This variation was excluded since such a voltage fluctuation was not permissible under the operative conditions and very especially so during periods of the observation of i and i'. The discontinuous character of the above curves suggest, therefore a methodic feature in the behaviour of the system due to aging under electrical excitation.

RESULTS AND DISCUSSION

A consideration of the curves showing the time-variation of i in the ozonisers 1 and 2 (which are but typical of several such series obtained) indicates 3 consecutive stages, *viz.*, (1) a rapid alteration in the conductivity of the discharge current in the initial stage it may be an increase or a decrease (2) an alternate rise and diminution of i with decreasing amplitude in the course of time showing a periodicity like behaviour and lastly (3) the attainment of a stationary conductivity

Similar phenomenon was observed in excited iodine vapour by Joshi and Bhutt and Deshmukh[8] and in bromine vapour by B B Prasad and Jathar[11] and by Deshmukh[10] and in chlorine by Deo[4]

This variation of the discharge current i with time at a constant exciting potential indicates that some surface or wall action is an operative factor Also under electrical discharge many physical reactions would take place including adsorption as well as desorption. Both processes may take place simultaneously or one

after another These would considerably alter the pressure and therefore the conductivity of the system and the variation of i would be a time reaction as d termined by the above factors. The explanation advanced by Joshi for the phenomenon observed in systems mentioned above is that of a formation and stabilisation of an adsorbed layer derived in part, from excited molecules and ions which according to him is also a chief seat of the photo-suppression of the discharge current. The process of adsorption alters the capacitance associated with the container walls and the gas phase consequently the conductivity is altered Associated with the instability of the formation of the adsorbed layer there is intermittent sorption and desorption or/and the production at the surface of the walls, of unstable intermediate products of discharge reaction,--all leading to a synchronous time ratio in the conductivity

The results now reported are in conformity with these suggesti ns. It is seen that *Joshi-effect* was observed in ozoniser 1 only after about 40 hours of exposure of the system to discharge and thereafter % Δi fl ctuated between 57 and 12 and became constant at the end of the experiment. This suggests the formation and eventuous stabilisation of an adsorbed layer Th breaks on the % Δi—time curve however are due to those in the time variation of i and of Δ (*cf* i_D, i_L curves in Fig. I) The production of Δi it may be noted is different from that of a change in the magnitude of i_D due to alteration in the capacitance associated with the walls and gas phase Joshi[1] has pointed o t that the latter is well a time process whereas th former has been shown to be from the measurements of time lag on the production of Δi an instantaneous process

In ozoniser 2, an appreciable initial decrease of is noticeable This may be du to a pressure reduction f th ystem by adsorption of the vapour by container walls. This corresponds to the well-known clean up phenomena. But in ozoniser 1 a slight initial increase is seen. Here the walls of the ozoniser are not blank due to pre-heat treatment *given which was simply* baking the ozoniser at about 200°C for about 4 hours. As a result of this, fine droplet of liquid mercury can be expected to cond nse on the surface and the adsorption of the vapour might have taken place even before starting th electrical discharge in th system.

In the explanation of the periodic phenomenon observed in $NO+H_2$ mixture and also in NO_2, Joshi[9] pointed out that the walls of the system under the influence of applied potential developed a strained condition and assumed that the duration of this strained condition and the time needed for recovery therefrom during the progress of discharge reaction is periodic and as a consequence a like change in the time rate of the discharge reaction is produced. *It is also pointed out that adsorption of* activated molecules and ions of limited life also takes place thus giving rise to instability in the capacitances associated with the container walls and the gas phase nd as a result the conductivity shows a time reaction. This second stage of the time-variation of i is explicable on this basis. It is however to be noted that to secure constant magnitudes of $_{m}i$ and % Δi a period of about 420 hours was taken which, in comparison with the aforesaid systems is excessively long This suggests that the process of sorption and desorption is slower with metallic vapours than with gases which is indeed the case as pointed out by Sherwood[12]

The results of the studies on hysteresis in *Joshi-effect* (which were carried out in a number of gases and vapours including mercury in these Laboratories) show that the surface action of the kind discussed above is compatible with its associated time lag Moreover the mechanism of Δ postulated much earlier by Prof Joshi for the phenomenon itself is consistent with such a surface action. He assumed three stages resulting in the production of Δi viz. (1) a boundary layer is formed on the container walls derived in part, from adsorption of ions and excited molecules under the applied fields, (2) photoelectric emission occurs from this boundary layer under external irradiation and (3) these photo-electrons are captured by the excited, neutral molecules to form slow moving negative ions which are responsible for the current decrease Δ as a space charge effect.

Now it was pointed out that adsorption of the vapour takes place under electrical discharge and this appears to be a short of chemisorption since Murty[13] has shown in chlorine that Δi under ageing progresses according to equation of first order reaction and the boundary l yer post lated by Joshi for stage (1) is therefore may well be chemical in nature That the electrical adsorption is chiefly of a chemical nature and not due to mechanical driving

in of the ions and molecules was shown by the work of Willows[1] and Hill[11] Further the phenomenon of adsorption of gases on solids is such a general one that it gives rise to characteristic effect in fields where this might not at first sight be expected as for example in the case of photoelectric and thermionic emission. S T Oregg [4] states that the work function in photoelectric emission is appreciably decreased if th mitter is adsorbed by foreign substances as for example when the strongly electro-positive metals like sodium potassi m etc., are adsorbed by platinum, molybdenum and tungsten The second assumption of Joshi s theory contemplates such a process followed by the formation of negative ions leading to photo-suppression of discharge current. The production of *Joshi effect* with but ordinary light in mercury vapour supports the above view since mercury vapour under normal conditions, (e. in th homogenous gas phase) is known to emit photo-electrons with only ultra violet light.

Our grateful th ks are due to Professor S. S Joshi D Sc. (London) F R. I. C F N I., Banaras Hindu University for his interest and advice

SUMMARY

The influence of 'aging at a constant exciting potential was investigated in mercury vapour employing a non-stop electrical discharge for about 440 hours. Th time variation of i_m, i and % Δ were studied wherein a discontinuous character was revealed which corresponded t the periodic ph nomena bserved in an ozoniser discharge in systems like NO_2, N_2O+H_2, Br_2, I_2 and Cl_2 by many investigators working in these Laboratories. The extent of discontinuities or fl ctuations in % Δi — time curves was five to ten times greater than a possible experimental error in the constancy of the exciting potential and therefore, they were taken to represent the methodic beh viour of th system. These results are discussed in the light of Joshi s theory for the mechanism of the *ffect* Δi and also of the periodic phenomena observed in systems mentioned above

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Studies on the composition of Ferrous Arsenate and Ferric Arsenite Part V Conductometric investigations on the composition of the so-called Ferric Arsenite (product of mixing $FeCl_3$ and $NaAsO_2$)

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In the previous parts of this series (part I and II, J I. C. S., 1948 25 447 1949 26 97–102) qualitative and quantitative analysis of the ferric arsenite compounds (obtained by mixing $FeCl_3$ nd $NaAsO_2$) were carried out elaborately to determine the composition of ferric arsenite. In this paper its composition has been investigated by conductometric titrations between the reactants at different dilutions. The titration curves yield two equivalence points suggesting the formation of two compounds of ferric arsenite on having the ratio of Fe As as 1 1 1 1 1 2 and the other in which the ratio of F As is nearly 1 2. The formation of both such compo nds has been supported by th nalytical results of the ferric arsenit precipitates (J I C S 1949 26, 99)

The composition of ferric arsenite according to the chemical equation should correspond to the formula $Fe(AsO_2)$ when ferric chloride is added sodium arsenite. B t in literature more complex and variable formulae have been given *e g.*, $6K_2O\ 5Fe_2O_3\ 9As_2O_3\ 24H_2O$ (Dobbin Pharm. J 1904, 4, 81 588) XF (OH)$_3$ YAs_2O (Oryng, Kolloid, Z 1916 22, 149) and F $_4As_2O_{11}$ $5H_2O$ or $3Fe_2O_3$, $Fe_2(AsO_3)_2$, $5H_2O$ (Bunsen and Berthold M llor "Treatise on Inorganic Chemistry 1929 Vol. IX p 133)

The possibility of mutual oxidation and reduction, was, however suggested by Jellinek and Winogradoff, (Z. Electrochem 19*4 30 477) according to the following equation,



$$2\,FeCl_3 + H_3\,AsO + H_2O \rightleftharpoons 2\,FeCl_2 + H_3AsO + 2\,Hcl$$

In view of the variations in the analytical results obtained by previous workers it was considered worthwhile to apply physico-chemical methods to throw further light on the composition of this complex compo nd. The results of only conductometric investigations have been incorporated and discussed in this paper

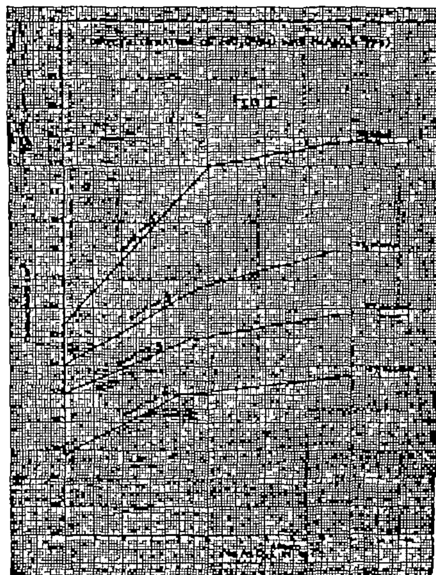
EXPERIMENTAL

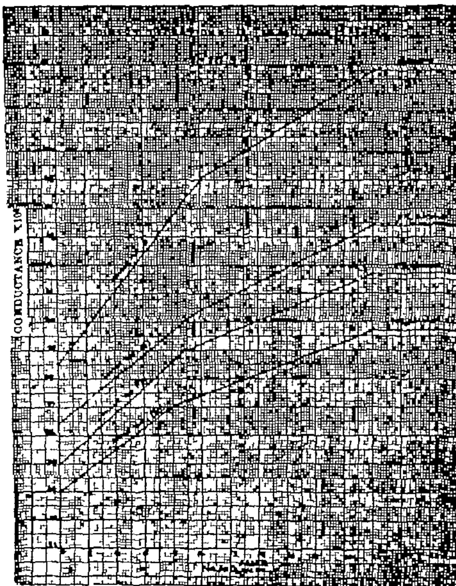
A. R. (B D H) reagents were used Standard sodium arsenite solution was prepared and estimated as described (Vogel 'Quantitative Analysis part III 104) Ferric chloride was estimated against dichromate using diphenyl amine as an indicator and also by Titanous chloride (Vogel 'Quantitative Analysis part III p 86) The conductivities were measured and corrected for the dilution effect as described in the previous publications (loc cit) Using different concentrations of the two salts in solution titrations were followed by the direct and the reverse methods (i. e wh n $NaAsO_2$ soln from the burette was added to 10c c of $FeCl_3$ soln. taken in the titration cell and vice-v rsa) The titrations were also performed in the presence of alcohol 2%, 5% and 10% by vol The corrected conductances were then plotted against the vol of the titrant and the equivalence points were determined by the points of intersection of the straight portions of the curves As all curves were similar only two figures have been given

It was observed that when aqueous solns. of $FeCl_3$ were mixed with neutralised $NaAsO_2$ soln no precipitate of ferric arsenite was obtained But when different amounts of M 5 sod. acetate was added to the mixture of the reactants, precipitation occurred with different colours and composition It was found that a thick precipitate of reddish yellow colour was formed when the PH value of $FeCl_3$ soln. is 3 03 and sodium arsenite is neutral (PH 6 95) Hence in each titration equivalent vol. of (say 10 c c of CH_3COONa for 10 c c of the soln. in the cell) sodium acetate was added in each titration The ferric arsenite formed is easily soluble in acetic acid and dil. NaOH soln. which shows that its formation depends upon H+ concentration of the reactants

Precipitation of ferric arsenite is almost instantaneous when $NaAsO_2$ is added to $FeCl_3$ soln. at suitable pH (3 63) but in the reverse process i. e when $FeCl_3$ is added to $NaAsO_2$, the precipitate does not readily come out on mixing the reactants. After some

time the mixture becomes colloidal and turbid the particles then gradually agglomerate and settle down It can be reasonably concluded that ferric arsenite adsorbs an enormous quantity of AsO_3 which peptises the precipitate as was also observed by Sen





(Jour Phys. Chem 1927 31 419). The reverse conductometric titrations therefore gave wid ly different results having very little constancy The results of direct titrations only have been incorporated

Having determined the titre values of sod arsenite required for a given vol of $FeCl_3$ in aqueous and also in alcoholic soln and on comparing them with the theoretical values calculated from the strengths of the solutions, conclusions regarding the composition of ferric arsenite formed under experimental conditions could be drawn. The influence of adsorption has been revealed from the difference of titre values in purely aq eous and aqueous alcoholic medium. A summary of observations has been given in th following tables :—

Composition of Ferric Arsenite by Conductometry

Table I

Conc of reactants		Aqueous sol tion F A	3% alcoholic solution F As	6% alcoholic solution F A	10% alcoholic solution F As
$FeCl_3$	N AsO_2				
M/4.7	M/4.9	1.1 97 1 96	1.1.985 1. 98	1...05 1 1.0	1:2.15 1 1 1
M/9 4	M/9.8	1 1.82 1. 96	1.1.86 1 98	1 1 92 1 1.0	1.2.05 1 1 1
M/14.1	M/14 7	1:2.0 1. 96	1.3.1 1 98	1.2 22 1 1 0	1:2.32 1 1.1
M/18 8	M/19 6	1:2.15 1 96	1:2.3 1. 96	1...4.. 1 1 0	1:2.5 1.1.1
M/9 4	M/4.8	1:2.0 1.1 0	1:2.1 1.1 1	1.2.2 1 1 06	1.2.32 1.1.2

Composition of Ferric Arsenite by inorganic analysis

(J I C. S., 1949 26 99)

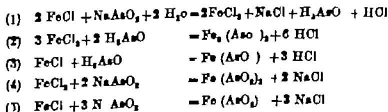
Table II

Con of reactants		FORMULA (Emperical)	F A
$FeCl_3$	$NaAsO_2$		
M/1 3	M/1 24 (aq solns.)	$Fe'''_{[illegible]}\ Fe_{1}\ (AsO_3)_{[illegible]}\ (AsO\ )$	1 1.8
M/25	M/25 (aq solns.)	$Fe'''_{[illegible]}\ Fe''\ (AsO)_{[illegible]}$	1 1.3
M/50	M/50 (aq solns)	$Fe'''_{[illegible]}\ Fe\ (AsO_3)_{[illegible]}$	1 1.2
M/1.3Aq	M/1.2 (neutralised)	$Fe'''_{1.6}\ Fe\ (AsO_3)\ (AsO\ )$	1:2.1
M/5	M/5 (neutralised)	$Fe'''_{[illegible]}\ Fe_{1.4}\ (AsO_3)_{[illegible]}\ (AsO\ )$	1 1 8
M/5 (Aged sample)	M/5 (neutralised)	$Fe'''\ Fe_{1.3}\ (AsO_3)_{7.3}\ (AsO_4)$	1.1 93

DISCUSSION

The analytical results (vide table II) show a wide variation of the ratio of total iron and arsenic in the ferric arsenite compounds formed by mixing different concentrations of ferric chloride and sodium arsenite but on close scrutiny the ferric arsenite com pounds can be divided into two classes, one having the ratio of Fe As as 1 *(1.2 to 1.3)* and the other in which the ratio of Fe As varies form 1 1.8 to 1.2.1 The results of conductometry (vide table I) confirm the formation of such compounds in which the ratio of Fe As is as 1 1 and 1:2 approximately

The variations in the composition of ferric arsenite compounds by analytical methods can be ascribed to many factors (a) adsorptive and hydrolytic character of the precipitated compound (b) H ion concentration of the reacting solutions (c) mutual oxidation nd reduction between the reactants In view of the above the follow ing machanism can be suggested for the reaction between FeCl and $NaAsO_2$.



(1) $2\ FeCl + NaAsO_2 + 2\ H_2O = 2FeCl_2 + NaCl + H_3AsO\ + HCl$

(2) $3\ FeCl_2 + 2\ H_3AsO = Fe_3\ (Aso\ )_2 + 6\ HCl$

(3) $FeCl\ + H_3AsO = Fe\ (AsO\ )\ + 3\ HCl$

(4) $FeCl_2 + 2\ NaAsO_2 = Fe\ (AsO_2)_2\ + 2\ NaCl$

(5) $FeCl\ + 3\ N\ \ AsO_2 = Fe\ (AsO_2)\ \ + 3\ NaCl$

The auther's grateful thanks are due to Dr Abani K Bhattacharya D Sc. Head of the Chemistry Department, Agra College Agra for his keen interest and guidance in this piece of investigation

9

COMPOSITION OF TURNBULL S BLUE (FERROUS FERRICYANIDE) BY CONDUCTOMETRIC METHOD PART II

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In continuation of my previous publications on the composition of Prussian Blue (J I.C.S. 1951 vol. 28 141 149 221–224, 703–709) this paper contains my observations on the composition of Turn bull's Blue (Ferrous ferri cyanide) by conductometric method. The results of titrations support the formation of two compounds KFeFe(CN) and $Fe_3[Fe(CN)_6]_2$ in aqueous and alcoholic solutions.

The composition of Turnbull's blue has been investigated by various a thors mostly by analytical methods and much light has been thrown on the intricacies of the reaction between ferrous sulphate nd potassium ferricyanide This reaction has been observed to suffer the effects of mutual oxidation and reduction in acid medium nd also the effect of adsorption and hydrolysis in excess f on or the other f the reactants. Hofmann Heine and Hochtlen (Annalen 1904 1-36) Muller and Stanish (Jour Prakt. Chem. 1909 (2) 79 81). No laborate physical method has been pursued systematically to elucidate the composition of such ferro-ferri cyanogen complexes. In this paper I have adopted conductometric method to throw furth r light on the composition of Ferrous ferricyanide (Turnbull's blue).

EXPERIMENTAL

Pure ferrous sulphate crystals were prepared by recrystallising from alcohol and dissolved in presence of dil. H_2SO Standard solutions of FeSO were prepared of several concentrations M/2 M/4, M/8

KMnO Well picked crystals (red) of $K_3Fe(CN)_6$ were taken and weighed to make standard solutions of strengths M/2, M/4, M/10 M/20 This was further checked by iodometric titrations in presence of ZnSO

The conductivities were measured by Kohlrausch Universal Bridge in the usual manner The titration cell was immersed in a thermostat to control the temp within + 1°C Direct titrations were carried out by adding FeSO to $K_3Fe(CN)$ in the titration cell and rev rse titrations were performed by adding K Fe $(CN)_6$ to FeSO The observed conductance *after each addition* was corrected for the dilution effect by multiplying it by the factor V/10 where V c c is the total volume of the solution in the titration cell and 10 c. c refers to the volume originally taken. (Davis "The conductivity of solutions p 238) Curves were plotted between the corrected conductance gainst the vol of the titrant. The equivalence point was obtained as a point of intersection of the two portions of the curves Titrations were also done in the presence of alcohol upto total concentration of 20% by volume

The experimental observations of conductometric titrations have been given in the following tables and the curves were plotted for determining the points of equivalence to ascertain the composi tion of Ferrous ferri cyanide

DIRECT TITRATIONS

When FeSO sol tion from the burette is added to $K_3Fe(CN)$ solution in the titration cell.

Table I

Vol. of M/*0 $K_3Fe(CN)_6$ soln. = 10 c. c Alcohol = nil (Fig. 1 curve 1)

M/4 FeSO added	Total Vol.	Corr Condy (mh)	M/4 FeSO added	Total V l.	Corr Condy (mh)
0 0 c c.	10 c c.	$58 8 \times 10^{-6}$	2.4 c c	12.4 c c	$55 0 \times 10^{-6}$
1.0	11 0	57 2	2.8	12.8	58 0
1 4	11 4	55.75	3 0	13 0	59 8
1.8	11.8	54.0	3 4	13 4	64.2
2.0	12.0	53.1	4 0	14 0	73.2

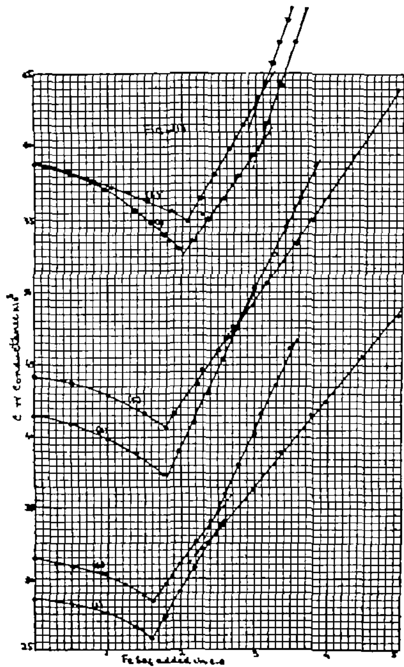


Table II

Vol. of M/20 $K_3Fe(CN)_6$ soln.=9c. c. Alcohol=1c c (Fig 1 Curve 2)

M/4 FeSO added	T tal V l	Corr Condy (mho)	M/4 FeSO added	T tal Vol	Corr Condy (mh)
0.0 c. c	10 c c	41.5×10^{-3}	2.6 c c	1*.6c. c	45.2×10^{-3}
1 0	11.0	40 0	3 0	13 0	49 0
1 4	11 4	39 0	3 4	13 4	5_0
1.8	11 8	37 5	3 6	13 6	53 2
2.2	12.2	41 0	4.6	14 6	60 5

Table III

Vol. of M/20 $K_3Fe(CN)_6$ soln =8c c Alcohol=2c c (Fig 1 Curve 3)

M/4 FeSO added	T tal V l	Corr Condy (mh)	M/4 FeSO added	Total V l	Corr Condy (mh)
0.0c. c	10 0c c.	$23\ 6\times10^{-3}$	*_c c	1_2c c	$30\ 8\times10^{-3}$
1 0	11 0	*7 7	2 4	1_4	32.5
1 4	11 4	?6 3	2.8	1* 8	35 0
1 6	11 6	?6 0	3 4	13 4	39 0
1 8	11 8	26.5	4 0	14 0	4 5

Table IV

T tration between M/8 FeSO soln. and M/ 0 $K_3Fe(CN)$ sol

Vol. of M/20 K F (CN)$_6$ soln.=10 c c Alcohol=Nil (Fig. 1 Curve 4)

M 8 FeSO added	Total Vol.	Corr Condy (mho)	M 8 F SO added	Tot l V L	Corr Condy (mh)
0 0 c c.	10 c c.	$58\ 3\times10^{-3}$	4.4 c c	14.4 c c	$56\ 5\times10^{-3}$
1 0	11 0	58.0	5 0	15 0	58 8
2.0	1_0	57 1	5 6	15 6	61 4
3 0	13 0	56.2	6 0	16 0	63 0
4 0	14.0	54 9	7 0	17 0	60 5

Table V

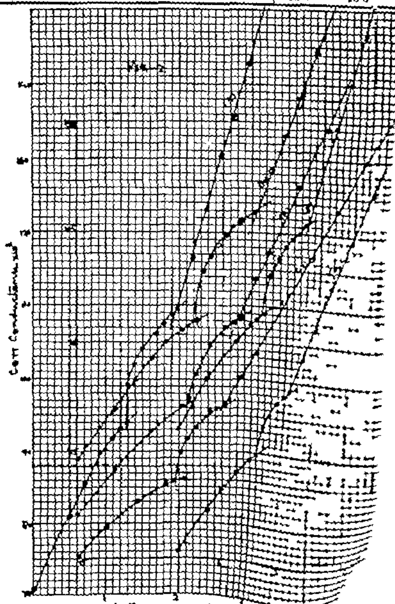
Vol of M/?0 $K_3Fe(CN)_6$ soln.=9 c.c Alcohol=1 c.c. (Fig.1 Curve 3)

M/8 FeSO added	T tal V l	Corr Condy (mho)	M/8 F SO added	T tal Vol	Cor Condy (mho)
0 0 c c	10 c c	44.0×10^{-3}	4 0 c c	14 0	$4\ \ 6\times10^{-3}$
2.0	12.0	42.5	4 4	14.4	43.5
3 0	13 0	41.5	5 4	15 4	4 .5
3 4	13.4	40.8	6 0	16 0	50 1

Table VI

Vol. of M/20 $K_4Fe(CN)_6$ soln. = 8 c.c. Alcohol = 20 c.c. (Fig. 1 Curve 6)

M/8 FeSO added	Total Vol.	Corr Condy (mho)	M/8 FeSO added	Tot l Vol.	Corr Condy (mho)
0.0 c.c.	10.0 c.c.	31.5×10^{-4}	4.0 c.c.	14.0	31.0×10^{-4}
1.5	11.5	30.4	4.6	14.6	33.0
2.5	12.5	29.5	5.0	15.0	[illegible]
3.4	13.4	28.7	6.0	16.0	40.0



REVERSE TITRATIONS

When K Fe (CN) soln. from the burette is added to FeSO soln in the tit ation cell

Table VII

Vol of M/20 FeSO soln =10 c. c. Alcohol=nil (Fig. 2 Curve 7)

M/4 K F (CN) added	Total Vol.	Corr Condy (mh)	M/4 K F (CN) added	Total V l	Corr Condy (mh)
0 0 c c.	10 c c	71.1×10⁻⁶	1.6 c c	11.6 c c.	105 0×10⁻⁶
0 5	10 5	81 0	2.0	12 0	109 1
1 0	11.0	90 0	2 4	12.4	123 0
1 3	11 3	99 1	3 0	13 0	137 0

Table VIII

Vol. of M/20 FeSO soln =9 c c. Alcohol=1 c c (Fig. 2 Curve 8)

M/4 K F (CN) added	Total V l	Corr Condy (mho)	M/4 K F (CN) added	T tal Vol.	Corr Condy (mh)
0 0 c c	10 c c	48 0×10⁻⁶	1 2 c c	11.2 c c.	63.9×10⁻⁶
0 4	10 4	54 9	1 6	11 6	74 1
0 8	10 8	60 0	1 8	11 8	76 0
1 0	11 0	62.1	2.6	12 6	101.2

Table IX

Vol of M/20 $FeSO_4$ soln.=8 c c Alcohol=2 c.c (Fig. 2 Curve 9)

M/4K F (CN)6 dded	T tal V l.	Corr Condy (mh)	M/4 K F (CN)	T tal V l.	Corr Condy (mho)
0 0 c c	10 0 c c	31.5×10⁻⁶	1.3 c.c.	11.3 c.c	50 0×10⁻⁶
0 4	10 4	36 3	1 6	11.6	53.5
0 8	10.8	42.0	2.0	12 0	62.0
1 1	11.1	44.5	2 8	12 8	80 0

Table X

Titrations between M/8 $FeSO_4$ soln and M/2 $K_4Fe(CN)_6$ soln.

Vol. of M/8 $FeSO_4$ soln. = 10 c. c. Alcohol = nil. (Fig. 2 Curve 10)

M/2 K_4F (CN) added	Total Vol.	Corr Condy (mho)	M/2 K_4F (CN) added	Total Vol.	Corr Condy (mho)
0 0 c c	10 c c	44.3×10^{-6}	2 0 c c	12 0	$105 0\times10^{-6}$
1 0	11 0	70 9	2 4	12 4	111 4
1 4	11 4	79 0	2 8	12 8	133.2
1 6	11 6	81 4	3 4	13 4	163 2
1 8	11 8	99 1	4.0	14 0	192.2

Table XI

Vol of M/8 $FeSO_4$ soln = 9 c c Alcohol = 1 c c (Fig 2 Curve 11)

M/2 K F (CN) added	Total V l.	Corr Condy (mh)	M/2 K F (CN) added	Total Vol.	Corr Condy (mho)
0 0 c c	10 0 c c	$27 7\times10^{-6}$	2 c c	12 0	$80 0\times10^{-}$
1 0	11 0	50 6	2 2 c c	12.2	82 0
1 5	11 5	59 0	2 6	12 6	100 8
1 8	11 8	75 0	3 0	13 0	118 0

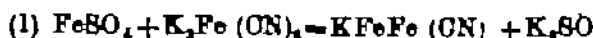
Table XII

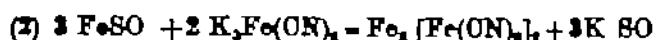
Vol of M/8 $FeSO_4$ soln. = 8 c. c Alcohol = 2 c. c (Fig. 2 Curve 1)

M/2 K F (CN) added	Tot l Vol.	Corr Condy (mh)	M/2 K F (CN) added	Total V l.	Corr Condy (mh)
0 0 c c	10 0 c c	$16 6\times10^{-6}$	1 8 c c	11 c c	$57 0\times10^{-6}$
0 8	10 8	33.2	2 0	12 0	58 8
1 2	11 2	36 2	2 4	12 4	73 0
1 4	11 4	45 0	3 6	13 6	113 0

DISCUSSION

Ferrous sulfate and potassium ferricyanide react in two ways:-


(1) $FeSO_4 + K_3Fe(CN)_6 = KFeFe(CN)_6 + K_2SO_4$


(2) $3 FeSO_4 + 2 K_3Fe(CN)_6 = Fe_3[Fe(CN)_6]_2 + 3K_2SO_4$

Taking into consideration the strength of solutions of $FeSO_4$ (M/5) and $K_3Fe(CN)_6$ (M/20) the calculated titre values for 10 c c of $K_3Fe(CN)_6$, for the formation of compounds $KFeFe(CN)_6$ and $Fe_3[Fe(CN)_6]_2$ in direct titration should be 7.5 and 5 c. c. respectively In the reverse titration the theoretical values can be calculated accordingly

In the direct titration when $FeSO_4$ is added from the burette) the change in conductivity is due to the formation of one molecule of K_2SO_4 from one molecule of $K_3Fe(CN)_6$ according to equation 1 and of three molecules of K_2SO_4 from two molecules of $K_3Fe(CN)_6$ according to equation No 2 the conductivity of the insoluble complex assumed to be zero

From the values of known ionic conductivities, it is anticipated that the conductivity should at first decrease as ferrous sulphate is added from the burette into potassium ferricyanide in the titration cell and th n increase after the equivalence point This ha been actually observed (curves 1 to 6)

In the reverse titration the total change in conductivity will be due to the conversion of ferrous sulphate in the cell into the insoluble complex (conductivity assumed to be zero) and to on molecule of K_2SO_4 according to equation 1 and of three molecules of ferrous sulphate into the insoluble complex and three molecules of K_2SO_4 according to equation 2. Calculated from the ionic conductivities, there should be a f ll in conductivity also but our actual observations from curve 7—12 are that there is a gradual rise in conductivity through out the titration, although the breaks do appear at the *significant points* This continuous *increase* can be explained as being due to the presence of dil sulphuric acid which had been added to ferrous sulphate for making the standard solution

With a view to study the discrepancy between the theoretical and observed titre values a summary of observations in aqueous and alcoholic solutions is given below for ready reference:—

DIRECT TITRATION

$FeSO$ soln. from the bu ette is added t K_3Fe (CN) in the cell.

$K_3Fe(CN)_6$	FeSO	Points of equivalence: Aqueous solns. Calculated	Observed	Alcoholl solns. Calculated	Observed	Formula supported
M/20	M/4	2 c. c	2.1	1.8	1.85 in 10% alcohol	$KFeFe(CN)_6$
				1 6	1.60 in 20% alcohol	
		3 c c.	3.15	2 7	2.8 in 10% alcohol	$Fe_3[Fe(CN)_6]_2$
				2 4	2.4 in 20% alcohol	
M/20	M/8	4 c c.	4 1	3.6	3 65 in 10% alcohol	$KFeFe(CN)_6$
				3.2	3.20 in 20% alcohol	
		6 c c	6 15	5 4	5.5 in 10% alcohol	$Fe_3[Fe(CN)_6]_2$
				4.8	4.85 in 20% alcohol	

REVERSE TITRATION

K_3Fe (CN) was added from the burette to $FeSO_4$ in the titration cell

$K_3Fe(CN)_6$	FeSO	Points of equivalence: Aqueous solns. Calculated	Observed	Al ohols solns. Calculated	Observed	Formula supported
M/4	M/20	2 c. c.	1 90	1.8	1.75 in 10% alcohol	$KFeFe(CN)_6$
				1 6	1 6 in 20% alcohol	
		1.33	1.25	1.2	1 15 in 10% alcohol	$Fe_3[Fe(CN)_6]_2$
				1.1	1.1 in 20% alcohol	
M/2	M/8	2.5c. c.	2 4	2.25	2.20 in 10% alcohol	$KFeFe(CN)_6$
				2 0	2.0 in 20% alcohol	
		1.66c c.	1.58	1.50	1.45 in 10% alcohol	$Fe_3[Fe(CN)_6]_2$
				1.33	1.30 in 20% alcohol	

It will be clear from the above table that in direct titration in aqueous medium the points of equivalence as observed from the curves are a bit higher than the theoretical values whereas in the reverse titrations they are slightly lower than the calculated ones. By the addition of alcohol in increasing proportion, the observed values tend to approach the calculated ones These results indicate the phenomenon of hydrolysis that seems to play a part in the case of Turn bull s blue The addition of alcohol suppresses the hydrolysis with the result that the observed values tend to have a closer approach to the theoretical ones

Phenomenon of adsorption also seems to play its role and the discrepancies may also arise on account of this If the adsorption of ferrous ions by Turn bull s blue is greater than that of ferricyanogen ions similar results may follow Experimental work on hydrolysis and adsorption by Turnbull's blue is already in progress with a view to throw further light on its composition

The conductivity curves in the case of direct and reverse titrations suggest the possibility of two compounds $KFeFe(CN)_6$ and $Fe_3[Fe(CN)_6]_2$. The curvature of the cur es in the vicinity of the points of intersection can be explained on the basis of adsorption of the ion by the precipitated complex as a result of which the total conductivity will slightly decrease as the quantity of the precipitated complex increases. Since the reaction indicated by the first portion of the curve differs f om the second one the shape of the middle portion of the curve will slightly vary from the former because the ionisation adsorption and hydrolytic behaviour of the compound formed at the well marked stages will be different from each other

The concentration of the reactants does not appreciably change the nature of observations The addition of alcohol contributes to control hydrolysis and also adsorptive properties

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Note —My grateful tha ks are d t Dr A K. Bhattacharya of Agra C llege for his kind interest in this investigation.

10

POTENTIOMETRIC STUDIES ON THE COMPOSITION OF TURNBULL S BLUE (FERROUS FERRICYANIDE) PART III

By

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The composition of Turnbull's blu has been investigated by the method of potentiometri titration between ferrous sulfate and potassium ferricy nide at several dilutions of these reactants By direct titrations the compositi n of ferrous ferricy nide corresponds to KFe [F $(CN)_6$] allowing for adsorption and hydrolysis whereas by the reverse titrations the formula of the compound comes out more correctly as $KFe[Fe(CN)_6]$

In continuation of my previous publication on th composition of Turnbull's blue by therm metric method (Jour Indian Chem, Soc., 1952 Vol 29 529) ttempts have been made to substantiat these observations by potentiometri method and the results have been incorporated and discussed in this paper

EXPERIMENTAL

Th reagents used were of Anala R (B D H.) quality Standard solutions of potassium ferricy nid and ferrous sulf te were prepared (1 oc cit) Electrode used was of platinised platinum (Muller Z physical Chem 1914, 88 44) and it was used in conjunction with a saturated calomel electrode Using the different concentrations of the two salts in solutions, the titrations were followed by th direct and the reverse methods i. e when ferrous sulfate solution was added from the burette to potassium ferri cyanide solution in the electrode vessel and vice versa.

The experimental observations of the potentiometric titrations have been given in the following tables and the curves have been plotted to determine the points of equivalence and to ascertain the composition of ferrous ferricyanid

DIRECT POTENTIOMETRIC TITRATIONS OF $FeSO_4$ and $K_3Fe(CN)_6$

When $K_3Fe(CN)_6$ soln is taken in the electrode vessel, and $FeSO_4$ soln. is added from the burette.

Table I

Vol. of M/20 $K_3Fe(CN)_6$ solution = 20 c.c. (Curve 1)

M/5 FeSO₄ added	E (obs)	M/5 FeSO₄ added	E (obs)	M/5 FeSO₄ added	E (obs)
0.0 c.c.	0.2745 volt	4.0 c.c.	0.2540 volt	5.8 c.c.	0.2525 volt
0.5	0.2715	4.5	0.2515	6.0	0.2535
1.0	0.2691	4.8	0.2500	6.2	0.2545
1.5	0.2660	5.0	0.2490	6.5	0.2555
2.0	0.2645	5.1	0.2485	7.0	0.2570
2.5	0.2610	5.2	0.2480	7.5	0.2580
3.0	0.2590	5.3	0.2475	8.5	0.2605
3.5	0.2565	5.5	0.2505	9.5	0.2850

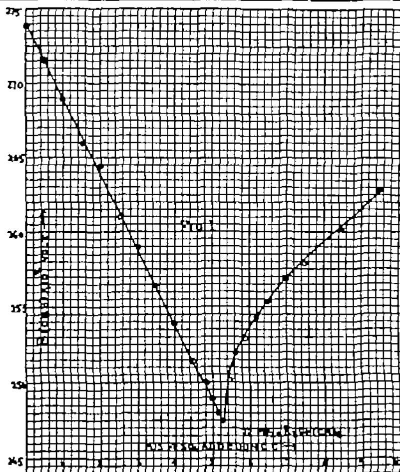


Table II

Vol. of M/10$K_4Fe(CN)_6$ soln.=10 c.c (Curve 2)

M/10 FeSO added	E (obs)	M/10 FeSO added	E (obs)	M/10 FeSO added	E (obs)
0.0 c.c.	0.2885 volt	6.5 c.c.	0.2630 volt	10.5 c.c.	0.2535 volt
1.0	0.2845	7.0	0.2615	11.0	0.2540
2.0	0.2800	7.5	0.2600	11.5	0.2555
2.5	0.2780	8.0	0.2580	12.0	0.2565
3.0	0.2760	8.5	0.2565	12.5	0.2575
3.5	0.2740	9.0	0.2550	13.0	0.2580
4.0	0.2720	9.5	0.2530	13.5	0.2585
5.0	0.2680	10.0	0.2515	14.0	0.2590
5.5	0.2665	10.2	0.2510	15.0	0.2600
6.0	0.2645	10.4	0.2512	16.0	0.2605
		10.6	0.2525	17.0	0.2615

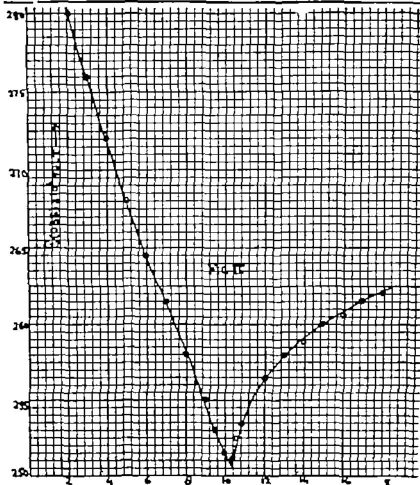


Table III

Vol. of M/20 $K_3Fe(CN)_6$ soln. = 20 c.c. (Curve 3)

M/10 FeSO added	E (obs)	M/10 FeSO added	E (obs)	M/10 FeSO added	E (obs)
0.0 c.c.	0.2735 volt	10.0 c.c.	0.2455 volt	13.5 c.c.	0.2535 volt
1.0	0.2710	10.2	0.2445	14.0	0.2540
2.0	0.2680	10.4	0.2440	14.5	0.2546
3.0	0.2650	10.6	0.2442	15.0	0.2552
4.0	0.2620	10.8	0.2455	15.5	0.2552
5.0	0.2595	11.0	0.2470	16.0	0.2560
6.0	0.2560	11.5	0.2495	17.0	0.2570
7.0	0.2535	12.0	0.2510	18.0	0.2576
8.0	0.2505	12.5	0.2520	19.0	0.2585
9.0	0.2485	13.0	0.2530	20.0	0.2595
9.5	0.2470				

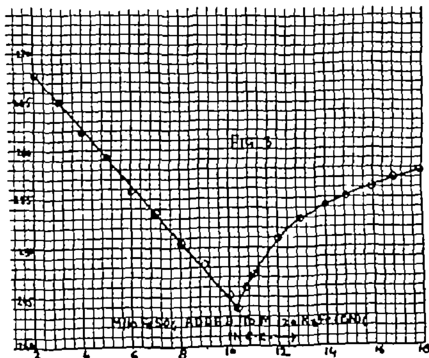
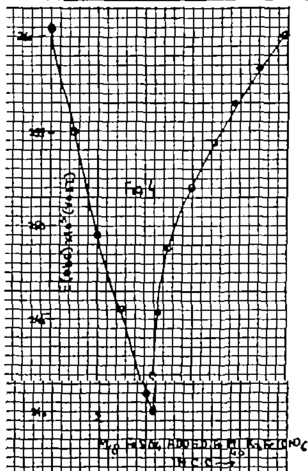


Table IV

Vol. of M/40 K. Fe (CN) soln =20 c. c. (Curve 4)

M/8 FeSO added	E (obs)	M/8 FeSO added	E (obs)	M/8 FeSO added	E (obs)
0-0 c.c.	0.2605 volt	3.8 c.c.	0.2418	6.6 c.c.	0.2538 volt
1.0	0.2550	4.0	0.2410	7.0	0.2545
1.5	0.2520	4.2	0.2400	7.5	0.2555
2.0	0.2495	4.4	0.2420	8.0	0.2565
2.5	0.2475	4.6	0.2455	9.0	0.2585
3.0	0.2455	5.0	0.2488	10.0	0.2600
3.2	0.2444	5.5	0.2505	11.0	0.2615
3.4	0.2435	6.0	0.2522	12.0	0.2630
3.6	0.2428	6.2	0.2528		
		6.4	0.2534		



REVERSE POTENTIOMETRIC TITRATIONS

When FeSO soln. is taken in the electrode vessel and $K_4Fe(CN)$ soln. is added from the burette.

Table V

Vol of M/20 $FeSO_4$ soln.=20 c.c (Curve 5)

M/5 K F (CN) added	E (obs)	M/5 K_4F $(CN)_6$ added	E (bs)	M/5 K F (CN) added	E (bs)
0.0 c.c.	0.3200 volt	2.8 c.c.	0.2945 volt	4 8 c.c.	0.2905 volt
0.0	0.3100	3.0	0 2935	5.0	0.2980
1.5	0.3045	3.2	0 2926	5.5	0.2935
2.0	0 3005	3 4	0.2922	6.0	0.2995
2.2	0.2985	3.6	0 2920	6.5	0.3030
2.4	0.2970	4.0	0 2917	7.0	0.3047
2.6	0.2957	4.5	0 2910	8.0	0.31 5
				9 0	0.3180

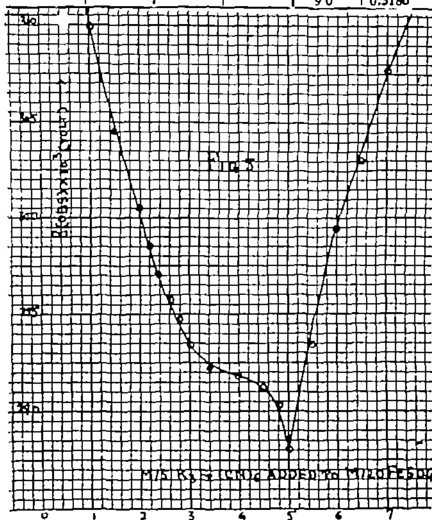


Table VI

Vol. of M/20 FeSO soln = 10 c.c. (Curv 6)

M/10 K F (CN) added	E (obs)	M/10 K F (CN) added	E (obs)	M/10 K F (CN)₆ added	E obs
0.0 c.c.	0.2825 volt	6.6 c.c.	0.2570	10.2 c.c.	[illegible]
01 0	0.2750	7.0	0 2570	10.6	0.2447
2.0	0.2695	7.5	0 2560	11.0	0.2450
3 0	0.2655	8.0	0.2523	11.5	0.24[illegible]5
4.0	0.2632	8.5	0.2495	12.0	0.2485
5.0	0.2605	9.0	0 2455	12 5	0 2495
5 5	0 2590	9.3	0 2435	13.5	0.2575
5.8	0 2580	9 5	0 2425	15.0	0.2545
6.0	0 2570	9 7	0.2430	16.0	0.2560
6.3	0 2570	10.0	0.2432		

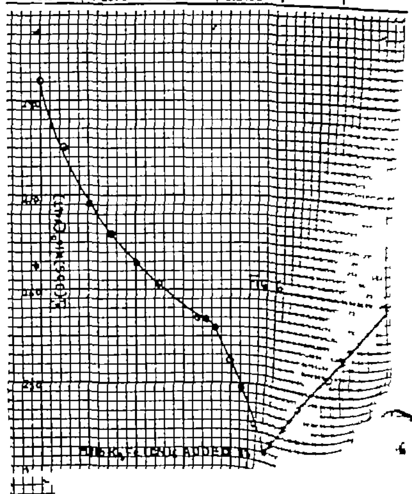


Table VII

Vol. of M/10 FeSO soln. =20 c.c (Curve 7)

M/5 K F (CN) added	E (obs)	M/5 K F (CN) added	E (obs)	M/5 K F (CN) added	E (obs)
0.0 c.c.	0.3230 volt	6.2 c.c.	0.3025 volt	10 c.c.	0.2990 volt
1.0	0.3180	6.4	0.3020	10.5	0.3005
2.0	0.3130	6.8	0.3015	11.0	0.3038
3.0	0.3105	7.2	0.3012	11.5	0.3070
4.0	0.3080	7.5	0.3012	12.0	0.3101
5.0	0.3060	8.0	0.3010	13.0	0.3145
5.5	0.3042	9.0	0.3010	14.0	0.3180
6.0	0.3036	9.5	0.3010		

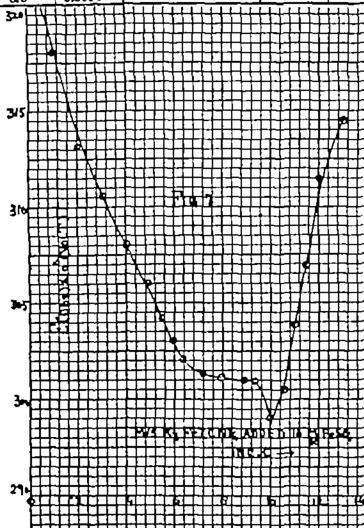


Table VIII

Vol of M/40 $FeSO_4$ soln.=20 c. c. (Curve 8)

M/8 $K_3Fe(CN)_6$ added	E (obs)	M/8 $K_3Fe(CN)_6$ added	E (obs)	M/8 $K_3Fe(CN)_6$ added	E (obs)
0.0 c.c.	0.2660 volt	2.6 c.c.	0.2434 volt	4.6 c.c.	0.2410
0.5	0.2580	2.8	0.2431	4 8	0.2430
1.0	0.2525	3.0	0.2428	5.0	0.2450
1.2	0.2500	3.2	0.2420	5.5	0.2480
1.4	0 2490	3.4	0.2410	6.0	0 2520
1 6	0 2470	3 6	0.2393	6.6	0.2550
1 8	0 2460	3.8	0.2370	7 0	0.2570
2.0	0 2445	4.0	0.2360	7 6	0.2600
2.2	0 2440	4 2	0.2380	8.0	0.2615
2.4	0 2435	4 4	0.2400		

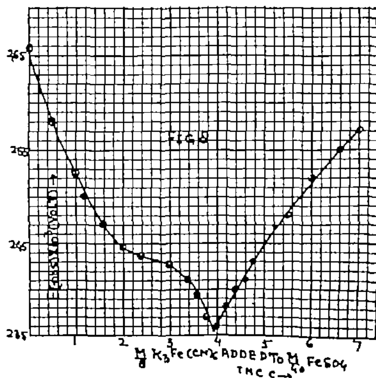


Table IX

RESULTS OF POTENTIOMETRIC TITRATIONS

DIRECT TITRATION

When $FeSO_4$ is added to $K_3Fe(CN)$ n the electrode vessel

Curves	FeSO	K_3F (CN)	T tre values for 10 c f the sol tion		for f rmation f compounds $F_3[Fe(CN)]_2$
			Observed from curves	lculated KF F (CN)	
1	M/5	M/20	5 3 c.c.	5 c.c.	7 5c.c
2.	M/10	M/10	10 4 c.c.	10 c.c	15c.c for10c.c.
3	M/10	M/20	10 4 c.c.	010 c.c.	15 c c
4	M/8	M/40	4 3 c c.	4 c c	5 c.c.

REVERSE TITRATIONS

When K Fe (CN) is added to $FeSO_4$ i the electrode vessel.

Curves	FeSO	K F (CN)	Titre values for 10 c. f the sol tion		for f rmat on of compounds F (Fe(CN))2
			bserved from curves	Cal ulated KF F (CN)	
5	M/20	M/ 5	5 c.c.	5 c c.	3 25 c.c.
6.	M/10	M/10	9.8 c c.	10 c c.	6 66c.c for10c.c
7	M/10	M/ 5	10.0 c.c.	10 c.c	6.6 c c.
8	M/40	M/ 8	3 90c.c	4 c c.	2 66 c.c.

DISCUSSION

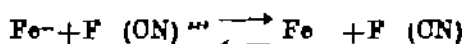
The general observation on the equivalence points is that the potentiometric titrations give only one point of equivalence in support of the formation of the compound $KFeFe(CN)_6$, which is formed by mixing the reactants in the ratio 1 1 in gram molecules In the direct titration (when FeSO is added to K Fe $(CN)_6$) the observed value is slightly higher than the theoretical one while in the reverse titration the observed and the calculated values almost exactly coincide

It may be observed that the nature of the titration curves obtained by the reaction of FeSO with $K_3Fe(CN)_6$ is unique There is no abrupt fall at the point of equivalence as is generally the case in potentiometric titrations On the other hand at the

point of equivalence the E. M F abruptly shoots up giving a clear indication of the point of equivalence Although it is difficult to venture any satisfactory expl nation of this observation, we consider that such behaviour may be possible at the point of equivalence when there are two different reversibl oxidation–reduction potentials set up in th course of a particular reaction Very few reactions of this type have been studied so far by potentiometric titration method and hence th re is hardly any reference of this type of curve in the literature

It is a known fact th t when a reducing substance acts on an oxidising agent parti ularly in presence of an acid and forms some insoluble compound the possibility of mutual oxidati n–reduction, how ver small it may be cannot be ignored In the case of formation of Prussian and Turnb ll's blue this fact has been referred to by Muller and Stannish (Jour Prakt Chem 1909 (2) 79 81) Hofmann, H ine and Hochtlen (Anal 1904, 1–36) Bhattacharya and Dhar (Zeit Anorg Ch m. 1933 213 240 248)

In the light of the above mutual oxidation and reduction oxidation potentials are set up as follows.—

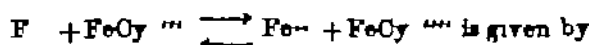


$$Fe^{\cdot\cdot} + F\ (CN)''' \rightleftharpoons Fe\ + F\ (CN)$$

On mixing the reactants, the system combines in itself two oxidation reduction potentials, one d e to the oxidation of ferrous ion and the other du to the reduction of Fe (CN) ''' The equilibrium potential of Fe· /Fe ·· and that of Fe(CN)6 /Fe(CN) ''' are the factors to control the change of potential at th point of eq ivalence

The drop of potential and its use may be explained as f llows:

The red–ox potential of the system



$$F\ + FeCy''' \rightleftharpoons Fe^{\cdot\cdot} + FeCy''''$$ is given by

$$E = E_o - \frac{RT}{nF} \log \frac{[Fe^{\cdot}\ ]\ [FeCy'''']}{[Fe\ ]\ [FeCy''']}$$

$$\text{or } E = E_o - \frac{RT}{nF} \log \frac{[Fe^{\cdot}\ ]}{[Fe\ ]} - \frac{RT}{nF} \log \frac{[F\ Cy'''']}{[FeCy''']}$$

or $E = E$

At the point of equivalence the arbitrary concentration ratios may be supposed to vanish when E = E

Now in the direct titration, K_4FeCy_6 is taken in the Cell and FeSO is added from the burette. It is, therefore likely that after the equivalence point has been crossed, the system retains only one part of the red-ox potential and can be expressed as

$$E = E_0 + \frac{RT}{nF} \log \frac{[Fe^{\cdot\cdot}]}{[Fe^{\cdot\cdot}]}$$

Hence, when Fe increases in the system the value of E goes on rising as is shown by the enclosed curves

In the reverse titration, the system reduces to

$$E = E + \frac{RT}{nF} \log \frac{[FeCy'''']}{[FeCy''']}$$ Hence on adding FeCy

ions from the burette after the point of equivalence a similar rise in potential occurs as in the former case

The loops in the reverse titrations seem to be due to the increased effects of adsorption. Experimental work is in progress to determine the exact reasons for the formation of such loops

ACKNOWLEDGEMENT

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11

DIAMAGNETISM OF OXALATE ION

By

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[Abstract: Diamagnetic susceptibility of powder crystals of Oxalic acid dihydrate and some inorganic oxalates have been measured by a modified Guoy method. The results are discussed in relation to resonance bonds in oxalate ions]

INTRODUCTION

Parallelism between diamagnetism and chemical saturation is a well established fact; hence for molecules with double bonds which show a high degree of unsaturation, λ in Pascal dditiv law $X_M = -X_A \cdot n + \lambda$ where X_M is the gram molec lar susceptibility of the molecule N is the number of toms in the molecule of susceptibility X_A and λ is the *constitutive correction*, should be large. This is borne out by experiments. It is found that double bonds in molecules behave lik paramagnetic carriers lowering the diamagnetic susceptibility This behaviour of molecules finds a ready explanation from Van Vleck's theory of polyatomic m lecules with zero spin The gram molec lar susceptibility of such molecules is given by (Van Vleck, 1935)

$$X_M = -\frac{Ne}{6mc}\Sigma\overline{\gamma} + \frac{2}{3}\Sigma\frac{m_1(n,n')}{h\gamma(n,n')}$$

Where $\gamma(n,n')$ = frequency corresponding to n, n' transition.

$m_0(n,n')$ = non diagonal element f the matrix for the angular momentum of the system

The first term of the expression is the well-known Langevin term The second term seems to be akin to the constitutive correction factor λ of Pascals Law and is positive like it.

In allphatic acids such as Formic and Acetic acids, the carboxyl group $-C\langle^{O}_{OH}$ which has double bond the value of the constitutive correction factor λ as deduced by Pascal is $+0.85 \times 10^{-6}$ suggesting that unsaturation arising out of double bonds lowers diamagnetism of molecules having zero spin.

It may be mentioned here that chemical unsaturation will produce differences in the directional magnetic properties of such molecules Indeed highly anisotropic diamagnetism of single crystal of Oxalic acid dihydrate has been reported by Lonsdale (1939). Hence it would be interesting to study magnetic anisotropy of single Oxalate crystals. The work on single crystals are in progress and it is proposed to report about them in a future communication.

The present communication deals with the measurement of powder values of some Oxalates discussed from the point of influence of double bonds on oxalate ions

EXPERIMENTAL

Chemicals used were of Merk's reagent quality recrystallised from aqueous solution at room temperatures.

The modified Gouy method as devised and used by Bose (1934) was adopted for the present measurements. The finely powered substance was nicely packed in a long pyrex test tube of uniform bore it was suspended from one arm of a sensitive balance, the lower end of the tube was at the centre of a strong homogeneous magnetic field while the upper part of it was well outside the field. The force acting on the powder column due to the magnetic field was compared with that of Naphthalene powder under identical conditions. A preliminary weighing of the empty test tube in the magnetic field supplied the necessary corrections for the container

If $\triangle W$ is the difference of weight of the test tube with powder substance (with the field on and off), $\triangle W$ be that due

to naphthalene powder and test tube and $\triangle W$ be that due to test tube alone then

$$\frac{\triangle W - \triangle W}{\triangle W - \triangle W} = \frac{k_s - k_a}{k_n - k_a}$$

where k_s is the volume susceptibility of powder substance

k_n is the volum susceptibility of Naphthalene powder

and k_a is the volume susceptibility of air

In actual experiment a current of five amperes were passed through the coils of th magnet producing a fi ld of about 10,000 Gauss, pole gap being one and one fourth f n inch This field produced a force of about 06 gm. on naphthalene powder

RESULTS

Results of mea urements are collected in table II. $\overline{X}$ represents mean mass susceptibility and X_M represents mean gram molecular susceptibility and are expressed in the usual units of 10^{-6} of a C G.S E.M. units.

The followi g values as recalculated by Myers (1952) from Angu s value using recent d ta for fundamental constants, were adopted for the evaluation of $\overline{X_M}$ for the oxalate group in various compounds. k_a was taken to be $+$ 0029 X 10^{-6} and k_n of naphthalene was taken to be 0.5318 X 10^{-6} (Krishnan and Banerji 1935)

Table I

ION	$-X_M$ X 10^{-6}
Na	3.7
K	12.8
Mg^{++}	2.8
Ca^{++}	10.2
Sr^{++}	19 7
Ba^{++}	30.9

Table II

Data refers to 30° C.

Serial No.	Substance	X	X_M	X_M for OxalateGr
1.	Oxalic acid dihydrate CooH CooH $+2\ H_2O$	4666	58. 8	27 0
2.	Ammonium Oxalate CooNH $CooNH_4 + H_2O$	4163	79 2	39 6
3	Sodium Oxalate CooNa CooNa	.2933	41. 6	37.20
4.	Potassium Oxalate CooK CooK $+H_2O$	5576	76 60	38 0
5	Magnesium Oxalate $(Coo)_2Mg, +2H_2O$	4564	67 6	38 8
6	Zinc Oxalate $(Coo)_2\ Zn, +2H_2O$	4097	77 60	38 2
7	Calcium Oxalate $(Coo)_2Ca$	.3460	44. 2	34. 1
8.	Strontium Oxalate $(Coo)_2Sr+H_2O$	.3490	67 6	33 9
9	Barium Oxalate $(Coo)_2Ba$	...	64. 9	34. 0

DISCUSSION

Oxalic acid dihydrate ($C_2H_2O_4 \cdot 2H_2O$) crystals have been studied by X-ray methods by Zachariasen (1934) and in greater details by Robertson and Woodward (1936) They find that the molecule $C_2H_2O_4$ is perfectly plane having the following interatomic distances as shown in the figure 1

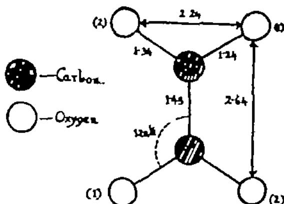


Fig — 1

It is of interest to note that both th oxygens attached to the Carbon tom are not precisely th same. The difference in the the interatomic distances of 1.34 A and 1.24 A is too small to distinguish between a C=O bond or a C—OH bond. It may be said that there is a partial resonance between the two bindings. Measurements of heats of formation in Carboxylic acids do indicate the existence of such resonance energy of about 25K Cal per molecule.

The very small C–C distance (1 43A°) as compared with 1.5A for single bond distance makes it clear that this C—C link is not a true single bond but must posses some amount of double bond character These two resonance effects will lower the diamagnetism of oxalate ion in oxalic acid dihydrate.

The value of X_M for oxalic acid dihydrate found by us compares favourably with that obtained by Lonsdale (1938) for single crystals. After making corrections for the two molecules of water and hydrogen otom X_M for the oxalate as given in table 2 is -27×10^{-6} as against $-.3 \times 10^{-6}$ from Lonsdale value If

in oxalate ion in oxalic acid dihydrate the above mentioned resonance effects were absent then $\overline{X}_M$ for such oxalate ion should be -38×10^{-6} as for C=C is -5.7×10^{-6} and for two O= is $-2 \times 2.75 \times 10^{-6}$

This is exactly the case with Oxalate ion in Ammonium Oxalate monohydrate X-ray studies by Hendricks and Jeffersons (1936) reveal that Oxal te molecule in Ammonium Oxalate monohydrate has definitely different from than that of oxalic acid dihydrate The C-C distance is large and is 1.58A as compared to 1.43A for Oxalic acid dihydrate This indicates the absence of C=C double bond again the CO groups are also not coplanar but inclined to one another at an angle of 28 degrees Thus in Ammonium Oxalate no resonance is present As a result its $\overline{X}_M$ should be near bout the value $38 \times 10^{-}$ On referring to table 2 we find its value is -39×10^{-6} agreeing well with the value deduced by us for no resonance

On referring to table 2 we find the structure of the oxalate ion in Na K Mg, and Zn Oxalates hould be like that of oxalate ion in Ammonium Oxalate as their X_M s centre round $-37 \times 10-6$ the value without the above two resonance effects. But in other oxalates namely Ca, Sr and Ba oxal tes the structure of th oxalate ion may be presumed to be like that of oxalic acid without C=C double bond so that λ in this case is +5.4 bringing down the value to -32×10^{-6} Hence the CO groups of oxalate ion in these salts will be Copl ner

Maleic acid (H C O) is also an open chain acid nd has double bond like Oxalic acid ($H_2 C_2 O$) hence it would be interesting to compare their diamagnetism Gray nd Birse (1914) give $\overline{X}_M$ for maleic acid as -49.5×10^{-6} Eliminating the contribution of two hydrogens and two carbons (which brings it to oxalic acid) X_M comes out to be -32×10^{-6} which is also the value for oxalic acid obtained by us

It is seen that for oxalic acid the second term of Van Vleck s expression, (equation 1) which may be indentified with λ has got a value comparable to the first term. Now this second term depends on the mean effective absorption frequency Thus a change of temperature effecting the refractive index or the substance should change the mean absorption frequency bringing

in a consequental change of diamagnetism of oxalic acid. This is not usually observed in diamagnetic substance. Probably χ in those substances is very small and hence the second term of Van Vleck's expression is ineffective Hence a study of the temperature variation of oxalic acid dihydrate may bring to light certain interesting points.

The work was carried out at the Physical laboratories, Birla College Pilani. The author wishes to express his thanks to its authorities for affording facilities for work and to Dr A. Mookerji, D Sc., for guidance and help

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Studies on the composition of Ferrous Arsenate and Ferric Arsenite. Part IV Conductometric investigations on the composition of the so called Ferrous Arsenate (product of mixing $FeSO_4$ and Na_2HAsO_4)

By

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The composition of the so called Ferrous Arsenate has been studied by the method of conductometric titrations between ferrous ammonium sulphate and disodium arsenate in aqueous and alcoholic medium. The direct titration curves suggest that the composition of ferrous arsenate nearly corresponds to the normal compound $Fe_3(AsO_4)_2$ in which the ratio of Fe As is 1 ·66. In the reverse case (when ferrous amm. sulphate from the burette is added to sod arsenate in the titration cell the compound obtained by conductometry is the one in which the ratio of Fe As is 1 1 1 The formation of both these compounds has been supported by the inorganic analysis of the ferrous arsenate precipitate (Bhattacharya, J I C S. 1949 26, NO 2, 103). The discrepancies from the theoretical ratio of Fe As are due to hydrolysis and adsorption effects

There is a meagre amount of literature on the subject and a few old references are available Hermann Metzke (Zeit Anorg Chem, 1899 19 457), William Dunkan (Pharm, Jour 1905 (IV) 20, 71) O Klemp and J Gyulai (Kolloid, Zeitsch 1917 15 202), The latest work is that of Bhattacharya (J I. C. S. 1949 26, 2 103) who analysed the precipitates (fresh and aged) obtained by mixing $FeSO_4$ add Na_2HAsO_4 at various concentrations and suggested

various emperical formulae His results suggested that the composition of the precipitated ferrous arsenate was influenced by (1) oxidation reduction phenomenon between the reactants (2) hydrolytic character of the compound (3) and phenomenon of adsorption which bring about complications in the analytical estimation of this compound.

In view of the difficulties associated with analytical work, attempts have been made in this paper to investigate the compound by physico-chemical methods which seem to throw further light on its composition Whil the results of potentiometric thermometric and amperiometric measurements are in progress, the results of conductometry are being communicated in this paper

EXPERIMENTAL

Merck's sample of Na_2HAsO 7HO was sed and the solution was standardised iodometrically against sodiumthio-sulphate of known strength Merck s sample of ferrous ammonium sulphate was recrystallised in alcohol and the dried sample was kept in the desiccator Its solution was standardised against KMnO as usual

The conductivities of solutions were measured as usual by Kohlrausch Universal Bridge (W G Pye Ltd.) The conductances were then corrected for the dilution effect (Davies 'The conductivity of solutions p 248) Using different concentrations of the two salts in solution titrations were followed both by the direct nd the reverse methods (i. e., when sod. arsenite from th burett w s added to ferrous ammonium sulphate in the titration cell and vice-versa). Th titrations were also carried out in presence of varying amounts of alcohol 2%, 5%, 10%. Th corrected conductances of the solution were then plotted against the titre and th equivalence point was noted by th intersection of th straight portions of the curves.

From the titration values I determined the ratio of Fe:As in these compounds nd compared them with those obtained by analysis (loc cit). Conductometric titrations were carried out t various concentrations of the reactants and a summary of results has been given in the following table for ready reference

Table I

DIRECT METHOD

When Na_2HAsO from the burette was added to Ferrous amm. sulphate in the titration cell

Con of the reactants	V l of F (ous) Amm. sulf te in the cell	Vol. f alcohol i the cell	V l (N HAsO req F Amm sul phat (btained from arves)
M/5.7 Fe (ous)	20 c c	0 0 c c	14.0 c.c
Amm sulphate	19 6	4	13 2
M/5 7 Na_2HAsO	19 0	1.0	13 1
	18.0	2.0	13 1
M/8 505 Fe (ous)	20 0 c.c	0 0 c c	14 0 c c
Amm sulphate	19 6	4	13.2
M/8 593 Na_2HAsO	19 0	1 0	13 0
	18 0	2 0	12.8
M/11 46 Fe (ous)	20 0 c c	0 0 c c	14.0 c c
Amm s lphate	19 6	4	13 2
M/11 40 Na_2HAsO	19 0	1 0	13 1
	18.0	2 0	13 1
M/21 5 Fe (ous)	20 0 c c	0 0 c c	14.0 c c
Amm sulphate	19 0	4	13.2
M/21 5 Na_2HAsO	19 0	1 0	13 1
	18 0	2 0	12 8

Table II

REVERSE METHOD

When Ferrous amm sulfate soln. was added from the burette to Na_2HAsO in the titration cell

Conc of reactants	Vol. f sod um arsenate sol taken	Vol of lcohol added	Vol f F (ous) Amm. lf te req (obtained from cur es)
M/5. Fe (ous)	20 0 c c	0 0 c c	19 0 c c
amm sulf te	19 6	0	18.0
M/5 7 Na_2HAsO	1..0	1 0	17 0
	18 0	2 0	10 0
M/8.505 Fe (ous)	20 0 c c.	0 0 c c	20 0 c.c
amm. sulfate	19 6	4	19 0
M/8 693 Na_2HAsO_4	19 0	1 0	18 0
	18 0	..0	17 0
M/11 46 Fe (ous)	20.0 c.c.	0 0 c c	20 0 c.c.
amm. sulfate	19.6	4	19 0
M/11 40 Na_2HAsO	19 0	1 0	18.2
	18.0	..0	17 1
M/21.5 Fe (ous)	20.0 c.c.	0 0 c.c	19 8 c c
amm sulfate	19 6	4	18.8
M/21.5 Na_2HAsO_4	19 0	1 0	18 0
	18 0	2 0	17.0

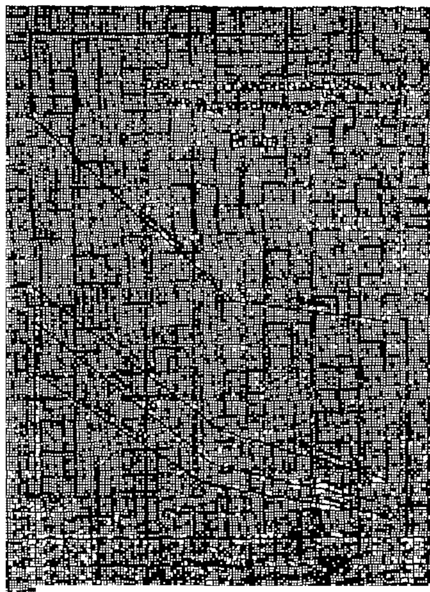
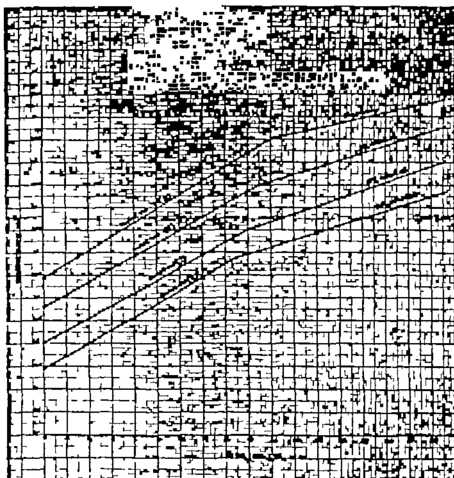


Table III

Composition of Ferrous Arsenate by conductometry (direct method)

Con of the rea tants F mm. Sol & N HAsO	Aqueous solution F As	5% alcoh lic soln. F A	8% alcohol soln F A	10% alcohol sol F : A
M/5 7 & M/5.7	1 7	1 674	1 608	1 66
M/8.595 & M/8 595	1 7	1 674	1 665	1 661
M/11 46 & M/11 46	1 7	1 674	1 670	1..663
M/21.5 & M 21.5	1 7	1 674	1 670	1 663



Composition of Ferrous Arsenate by conductometry (Reverse method)

Con of the reactants F amm Sot & N HA O4	Aqueous sol tion F As	5% alcoholic soln. F A	5% alcoh l sol F A	10% alcoh lic soln F A
M/5 7 & M/5 7	1 1 05	1 1 088	1 1 12	1 1 125
M/8.595 & M/8.595	1 1	1.1 03	1 1 055	1 1 059
M/11.46 & M/11 46	1 1	1 1.03	1.1.055	1.1.063
M/21 5 & M/21 5	1 1	1.1 03	1 1 055	1 1 058

Table IV

Composition of Ferrous Arsenate by Inorganic Analysis

(*Bhattacharya J.I C.S 1949* 26 *2, 103*)

Conc of the rea tants.	Formula	F A
1 Aq M/3.24 FeSO & neutral M/3.23 Na_2HAsO	$Fe''_{1.8}Fe$ $(AsO_3)_1(AsO_4)_3$	1 1.08
2. Acidified M/3 24 FeSO & neutral M/3 23 Na_2HAsO	$Fe_{14}(AsO_3)_1(AsO\ )_{12}$	1 1 06
3. Acidified M/6.86 FeSO & M/3.23 Na_2HAsO	$Fe_{24.2}(AsO_3)_1(AsO\ )_{27}$	1..92
4. Acidified M/5 FeSO & neutral M/5 Na_2HAsO	$Fe_{22.6}(AsO_3)_1(AsO\ )_{21.6}$	1 1.2
5 Acidified M/10 FeSO & M/10 neutral Na_2HAsO	$Fe_{21.6}(AsO_3)_1(AsO_4)_{22}$	1 1 1

DISCUSSION

It is observed that by adding ferrous ammonium sulphate to disodium hydrogen arsenate, greenish white precipitate is first formed which gradually assumes a dark green colou in 10 minutes time But in the reverse case when Na_2HAsO is added to ferrous ammonium sulfat the dark green precipitate is formed immediately It seems in the former case the colour change is due to the adsorption effect and slow hydrolysis.

The conductometric titration curves yield only one point of equivalence indicating the formation of only one compound In the case of direct titration the composition of ferrous arsenate nearly corresponds to the normal compound $Fe_3(AsO_4)_2$ in which the ratio of Fe As is 1 66 The curves in the reverse titrations suggest the formation of a compound in which the ratio of Fe As is nearly 1 1 1 which is supported by the analytical results obtained by Bhattacharya (J I. C. S., 1949 26 103) vide table IV In the presence or increasing amounts of alcohol the observed titre values gradually approach the theoretical values, because alcohol contributes to check hydrolysis and adsorption.

In view of the observations of conductometry and those of quantitative analysis, it can be reasonably concluded that the formation of ferrous arsenate is complicated by many factors, The role of P of the soln. adsorption, hydrolysis, and mutual oxidation and reduction are the most important factors which are responsible for the variation of the composition of the compounds formed under different conditions.

Note—The author's grateful thanks are due to Dr A K. Bhattacharya, D Sc f Agra College, Agra for his guidance.

STUDIES ON THE COMPOSITION OF CERIUM (CEROUS) FERROCYANIDE COMPLEX BY POTENTIOMETRIC METHOD

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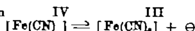
The composition of cerous ferrocyanide has been determined by potentiometry using th ferricyanide-ferrocyanid electrod The composition of the compound cerous ferrocyanide indicated by potentiometry is the ne corresponding to the molecular formula Ce [K Fe $(CN)_6$]. Th discrepancies in the equivale ce points from the theoretical values have been explained as being due to the adsorption of Ce''' ions by the precipitated complex. In th presence of 30% lcohol the titration curve has a regular shape nd the theoretical nd the observed titre values for the formation of the compl x Ce [K Fe $(CN)_6$] almost coin ide

In continuation of my previous commu ication to th J I C S entitled, The composition of cerous ferrocyanide by condu tometri m thod this paper contains my observations obtained by potentiometric titration.

According to the equation

$$\overset{IV}{[Fe(CN)\ ]} \rightleftharpoons \overset{III}{[Fe(CN)_6]} + \ominus$$

the oxidation potential of the f rricyanide-ferrocyanide electrod is given by



$$E = E + 0.059 \ln \frac{[Fe(CN)_6]'''}{[F\ (CN)_6]''''} \text{ at } 25°C$$

Solutions of Cerous nitrat were titrated against potassi m ferrocyanid at several concentrations of these reactants. Th reverse titrations only (When $K_4Fe(CN)_6$ from th burette was added t cerous nitrate in th beake) gave satisfactory results. $Fe(CN)_6$ /Fe(CN '''' electrode was prepared by dding a little 1% solution of potassi m ferricyanid to K $Fe(CN)_6$ sol (Gal tti Bull Soc Chim 1864, ii, 2, 83· Z. anal Chem. 1865 4, 213). In the titration of cerous nitrate with potassium ferrocyanide so l ng as there is an excess of Ce ''' ions in the sol tion the concentration of ferrocyanide is small and so the pot ntial of the lectrode is high Near th equivalence point when th cerous ions are quantit tively precipitated the next drop of ferrocyanide sol tion dded to cerous nitrate causes an increase in $[Fe(CN)_6]''''$ and h nce a decrease in th oxidation potential occurs The point of equivalence can therefore, be read from the potentiometric titration curves

EXPERIMENTAL

Merck s Anala R reagents were used, and standard solutions of Cerous nitrate and potassium ferrocyanide were prepared. In all the titrations potassium ferrocyanide containing 1% potassium ferricyanide was used (Kolthoff and Furman Potentiometric Titrations) Electrode used was of platinised platinum foil (Muller Z physical Chem., 1914 88, 44), and it was used in conjunction with a saturated calomel electrode. The titrations were also carried out in presence of alcohol upto a total concentration of 30% by volume Curves were plotted between the vol. of ferrocyanide added and the E (observed) and from the fall of the curves the equivalence point could be found out.

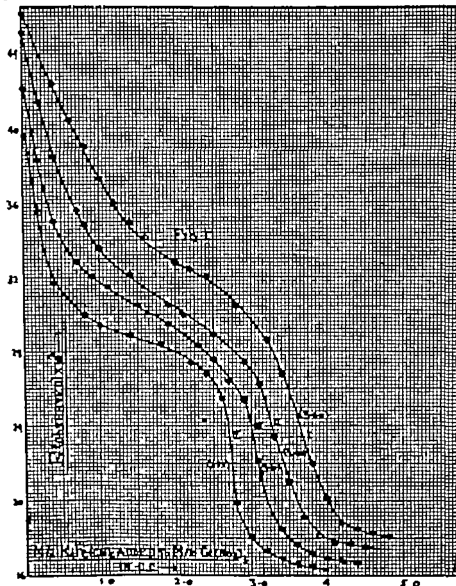


Table I

Conc. of K F(CN)$_6$ = M/2 Conc of Ce(NO$_3$) = M/10

Vol. of Cerous Nitrate taken = 20 c c
Alcohol added = Nil (Fig. 1 Curve 1)

K F (CN) added	E(obs)	K F (CN) added	E(obs)	K F (CN) added	E(obs)	K F (CN) added	E(obs)
0.0 c.c.	4612 volt	1 8	3350 volt	3.0 c.c.	2960 volt	4 2 c.c.	1884 volt
4	4240	2.0	.3280	3.2	2860	4 4	1850
8	.3892	2.2	3235	3 4	2680	4 6	1830
1 0	3722	2 4	.3191	3.6	2465	4 8	1815
1.2	3600	2.6	.3120	3 8	2205	5.0	1800
1 4	3505	2.8	.3045	4 0	2010	5 2	1790

Table II

Vol of M/10 Ce(NO$_3$)$_3$ taken 18 c c
Alcohol added = 2c c (Fig. 1 Curve 2)

K F (CN) added	E(obs)	K F (CN) added	E(obs)	K F (CN) added	E(obs)	K F (CN) added	E(obs)
0 0 c.c.	4514 volt	1 4 c.c.	3210 volt	2.7	.2820 volt	3 7 c.c.	1920 volt
2	4205	1 6	3138	2.9	2740	3 9	1822
3	4010	1 9	3055	3.1	.2621	4 1	1780
4	.3250	2.1	3000	3.3	2340	4 3	1758
6	3608	2.3	2950	3 5	2102	4 5	1762
1 0	3365	2.5	2890	3 7	1920	4.8	1740

Table III

Vol of M/10 Ce(NO$_3$)$_3$ soln. taken = 16 c c
Alcohol added = 4 c c. (Fig 1 Curve 3)

K F (CN) added	E(obs)	K$_4$F (CN) added	E(obs)	K F (CN) added	E(obs)	K$_4$F (CN) added	E(obs)
0 0 c.c.	4210 volt	9 c.c.	3203 volt	2 3 c.c.	2832 volt	3 4 c.c.	1840 volt
2	.3832	1 1	3150	2.5	.2760	3.6	1764
.3	3665	1 3	3100	2 7	2610	3 8	17 0
4	3504	1 5	3050	2.9	2542	4 0	1690
5	3400	1 7	3006	3 1	2208	4 2	1681
7	3232	1 9	.2950	3.2	2020	4 6	1650

Table IV

Vol of M/10 Ce (NO$_3$) soln taken = 14 c. c.
Alcohol added = 6c c (Fig 1 Curve 4)

K$_4$F (CN) added	E(obs)	K F (CN) added	E(obs)	K F (CN) added	E(obs)	K$_4$F (CN) added	E(obs)
0.0 c.c.	3960 volt	1 0 c.c.	2945 volt	2.0 c.c.	.2805 volt	3 2 c.c.	1730 volt
1	3605	1 2	2914	2 2	2745	3 4	1690
2	.3350	1 4	2890	2.4	2678	3 6	1662
4	3170	1 6	2868	2.6	2550	3 8	1640
.8	.3002	1.8	.2840	3 0	1790	4 0	1632

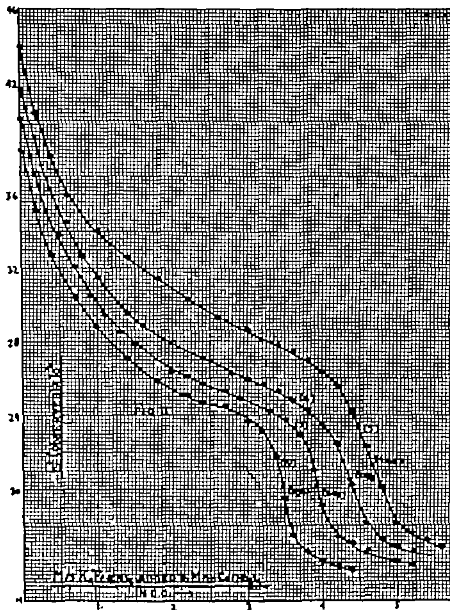


Table V

Titration between M/5 $K_4Fe(CN)_6$ and M/20 $Co(NO_3)_2$

Vol. of M/20 $Co(NO_3)_2$ soln. taken = 20 c.c.
Alcohol added = Nil (Fig 2 Curve 5)

$K_4Fe(CN)_6$ added	E (obs)	$K_4Fe(CN)_6$ added	E (obs)	$K_4Fe(CN)_6$ added	E (obs)	$K_4Fe(CN)_6$ added	E (obs)
0 0 c.c.	.4395 volt	1.6 c.c.	.3200 volt	3 6 c.c.	.2742	4.8 c.c.	.2014 volt
.2	.4042	1.8	.3150	3.8	.2695	5.0	.1840
.4	.3812	2.2	.3036	4 2	.2560	5 4	.1726
.8	.3500	2.6	.2930	4 4	.2420	5.6	.1685
1.2	.3330	2 8	.2890	4 6	.2224	6 0	.1646
1 4	.3258	3 2	.2920			6 5	.1600

Table VI

Vol of M/20 Co $(NO_3)_2$ = 18 c.c.
Alcohol added = 2 c.c (Fig. 2 curve 6)

$K_4Fe(CN)_6$ added	E (obs)	$K_4Fe(CN)_6$ added	E (obs)	$K_4Fe(CN)_6$ added	E (obs)	$K_4Fe(CN)_6$ added	E (obs)
0 0 c.c.	.4170 volt	1 4 c.c.	.2966 volt	3.0 c.c.	.2600 volt	4 2 c.c.	.2232 volt
.2	.3865	1 6	.2895	3 2	.2568	4 4	.2005
.4	.3612	2.0	.2791	3 4	.2537	4 6	.1810
.8	.3262	2.2	.2748	3 8	.2425	4 8	.1725
1 0	.3152	2.6	.2660	4 0	.2350	5 4	.1640

Table VII

Vol. of M/10 Co $(NO_3)_2$ taken = 16 c.c.
Alcohol added = 4 c.c (Fig. 2 Curve 7)

$K_4Fe(CN)_6$ added	E (obs)	$K_4Fe(CN)_6$ added	E (obs)	$K_4Fe(CN)_6$ added	E (obs)	$K_4Fe(CN)_6$ added	E (obs)
0.0 c.c.	.4020 volt	1 3 c.c.	.2836 volt	2 7	.2550 volt	3 9 c.c.	.2105 volt
.2	.3712	1.5	.2730	2.9	.2493	4.0	.1902
.5	.3380	1 7	.2732	3 1	.2460	4 2	.1740
.7	.3210	2.0	.2640	3.3	.2420	4 4	.1710
.9	.3052	2.2	.2612	3.5	.2376	4 6	.1670
1 1	.2948	2.4	.2570	3.7	.2300	4.8	.1645

Table VIII

Vol of M/10 Co $(NO_3)_2$ soln. taken = 14 c.c
Alcohol added = 6 c.c (Fig. 2 Curve 8)

$K_4Fe(CN)_6$ added	E (obs)	$K_4Fe(CN)_6$ added	E (obs)	$K_4Fe(CN)_6$ added	E (obs)	$K_4Fe(CN)_6$ added	E (obs)
0.0 c.c.	.3845 volt	1.2 c.c.	.2780 volt	2.8 c.c.	.2418	3.8 c.c.	.1664 volt
.2	.3518	1 6	.2608	3.0	.2374	4 0	.1612
.4	.3282	1.6	.2591	3.2	.2322	4 2	.1588
.6	.3113	2 0	.2544	3 4	.2160	4 4	.1560
.8	.2974	2.2	.2510	3.6	.1748	4.6	.1538
1 0	.2885	2 6	.2450			5.0	.1484

Table IX

Titration between M/15 $K_4Fe(CN)_6$ and M/50 $Ce(NO_3)_3$

Vol. of M/50 $Ce(NO_3)_3$ soln. taken=20 c.c.
Alcohol added=Nil (Fig. 3 Curve 9)

$K_4Fe(CN)_6$ added	E (obs)	$K_4Fe(CN)_6$ added	E (obs)	$K_4Fe(CN)_6$ added	E (obs)	$K_4Fe(CN)_6$ added	E (obs)
0.0 c.c.	.3660 volt	2.0 c.c.	.2855 volt	4.4 c.c.	.2583 volt	5.8 c.c.	.2006 volt
.2	.3638	2.4	2800	4.8	.2545	6.0	1940
.4	.3425	2.8	2758	5.0	.2480	6.2	1860
.8	.3142	3.2	2710	5.2	2420	6.4	1812
1.2	2995	3.6	.2675	5.4	.2305	6.6	1748
1.6	2920	4.0	.2610	5.6	.2100	6.8	1730

Table X

Vol. of M/50 $Ce(NO_3)_3$ soln. taken=18 c.c.
Alcohol added=2 c.c. (Fig. 3 Curve 10)

$K_4Fe(CN)_6$ added	E (obs)	$K_4Fe(CN)_6$ added	E (obs)	$K_4Fe(CN)_6$ added	E (obs)	$K_4Fe(CN)_6$ added	E (obs)
0.0 c.c.	.3590 volt	1.8 c.c.	.2750 volt	3.8 c.c.	.2518 volt	4.8 c.c.	.2362 volt
.2	.3432	2.2	2694	4.0	.2495	5.0	.2230
.4	.3270	2.6	.2646	4.2	2475	5.2	2060
.8	3018	3.0	2602	4.4	2435	5.4	1940
1.2	.2878	3.2	2581	4.6	2400	5.6	1862
1.6	.2760	3.4	2536			6.0	1780

Table XI

Vol. of M/50 $Ce(NO_3)_3$ soln. taken=16 c.c.
Alcohol added=4 c.c. (Fig. 3 Curve 11)

$K_4Fe(CN)_6$ added	E (obs)	$K_4Fe(CN)_6$ added	E (obs)	$K_4Fe(CN)_6$ added	E (obs)	$K_4Fe(CN)_6$ added	E (obs)
0.0 c.c.	.3465 volt	1.8 c.c.	2510 volt	3.6 c.c.	.2435 volt	4.8 c.c.	1920 volt
.2	3310	2.2	2605	3.8	2420	5.0	1850
.4	.3120	2.6	.2565	4.0	2390	5.2	1800
.8	2910	2.8	2540	4.2	2340	5.4	1780
1.2	2770	3.2	2480	4.4	2280	5.6	.1750
1.5	2705	3.4	.2835	4.6	.2125	6.0	1720

Table XII

Vol. of M/50 $Ce(NO_3)_3$ soln. taken=14 c.c.
Alcohol added=6 c.c. (Fig. 3 Curve 12)

$K_4Fe(CN)_6$ added	E (obs)	$K_4Fe(CN)_6$ added	E (obs)	$K_4Fe(CN)_6$ added	E (obs)	$K_4Fe(CN)_6$ added	E (obs)
0.0 c.c.	.3265 volt	2.0 c.c.	2490 volt	3.4 c.c.	.2360 volt	4.2 c.c.	1890 volt
.2	.3030	2.4	2450	3.6	.2335	4.4	1760
.6	2815	2.8	2430	3.8	2285	4.6	1720
1.0	2660	3.0	2410	4.0	2200	4.8	1700
1.6	2540	3.2	2395		——	5.2	1670

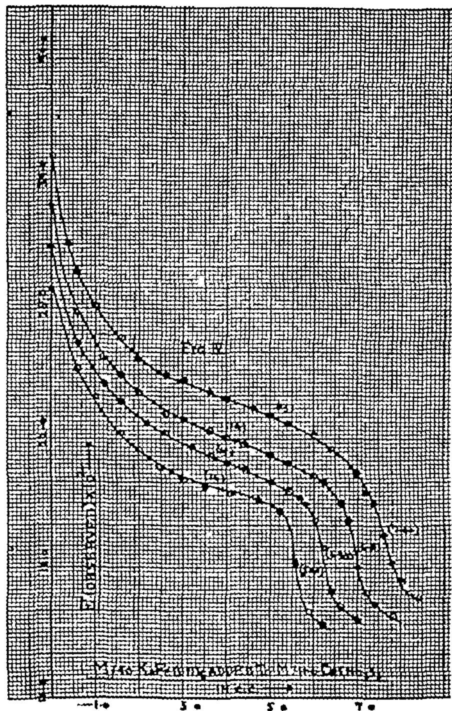


Table XIII

Titration between M/40 $K_4Fe(CN)_6$ and M/100 $Ce(NO_3)_3$ solution

Vol. of M/100 $Ce(NO_3)_3$ soln. taken = 20 c. c.
Alcohol added = Nil (Fig. 4 Curve 13)

$K_4Fe(CN)_6$ added	E (obs)	$K_4Fe(CN)_6$ added	E (obs)	$K_4Fe(CN)_6$ added	E (obs)	$K_4Fe(CN)_6$ added	E (obs)
0.0 c.c.	3510 volt	2.6 c.c.	.2505 volt	5.4 c.c.	2270 volt	7.4 c.c.	1825 volt
.4	3105	3.2	.2455	5.8	2240	7.6	1760
.8	.2880	3.8	2405	6.2	2180	7.8	1620
1.4	.2695	4.2	2370	6.4	2155	8.0	1540
1.8	2620	4.8	.2320	6.6	2120	8.2	1480
2.2	2560	5.0	2305	7.0	2040	8.6	1440

Table XIV

Vol. of M/100 $Ce(NO_3)_3$ soln. taken = 18 c. c.
Alcohol added = 2 c. c. (Fig. 4 Curve 14)

$K_4Fe(CN)_6$ added	E (obs)	$K_4Fe(CN)_6$ added	E (obs)	$K_4Fe(CN)_6$ added	E (obs)	$K_4Fe(CN)_6$ added	E (obs)
0.0 c.c.	.3280 volt	2.2 c.c.	2380 volt	4.2 c.c.	2185 volt	5.8 c.c.	2050 volt
.4	.2910	2.6	2325	4.6	.2160	6.2	2005
.8	.2690	3.0	.2290	4.8	2140	6.6	1905
1.2	2555	3.4	2235	5.0	.2120	6.8	1805
1.6	.2465	3.8	2220	5.2	2110	7.0	1620
1.8	.2440	4.0	.2200	5.4	2085	7.2	1490

Table XV

Vol. of M/100 $Ce(NO_3)_3$ soln. taken = 16 c. c.
Alcohol added = 4 c. c. (Fig. 4 Curve 15)

$K_4Fe(CN)_6$ added	E (obs)	$K_4Fe(CN)_6$ added	E (obs)	$K_4Fe(CN)_6$ added	E (obs)	$K_4Fe(CN)_6$ added	E (obs)
0.0 c.c.	.3085 volt	2.0 c.c.	2300 volt	4.0 c.c.	.2090 volt	5.8 c.c.	1900 volt
.2	.2870	2.2	.2275	4.4	2060	6.0	1825
.4	.2720	2.6	.2230	4.6	2040	6.2	1700
.8	.2565	2.8	.2205	4.8	2020	6.4	1480
1.2	.2455	3.2	2160	5.2	1980	6.6	1420
1.6	2360	3.6	.2125	5.4	1960	6.8	1375

Table XVI

Vol. of M/100 $Ce(NO_3)_3$ soln. taken = 14 c. c.
Alcohol added = 6 c.c. (Fig. 4 Curve 16)

$K_4Fe(CN)_6$ added	E (obs)	$K_4Fe(CN)_6$ added	E (obs)	$K_4Fe(CN)_6$ added	E (obs)	$K_4Fe(CN)_6$ added	E (obs)
0.0 c.c.	2890 volt	1.2 c.c.	2330 volt	3.5 c.c.	1985 volt	5.2 c.c.	1860 volt
.2	.2740	1.6	2225	3.8	1965	5.4	1815
.4	.2625	1.8	2180	4.1	1950	5.6	1580
.6	.2520	2.2	.2115	4.5	1930	5.8	1420
.8	.2440	2.5	2070	4.7	1920	6.0	1360
1.0	2100	3.0	2015	5.0	1890	6.4	1320

Table XVII

Summary of results of potentiometric titrations in aqueous and alcoholic medium

Fig	$K_4Fe(CN)_6$	Ce $(NO_3)_3$	P t obtained from Curves				Formula supposed
			Aqueous Cal	Sol observed	Alcoholic Calc	Sol observed	
1	M/4	M/10	4 0 c.c.	3 60 c c.	3 60	3 40 c c in 10% alcohol	Ce K
					3.2	3 10 in 20% alcohol	$[Fe(CN)_6]$
					2.8	2 75 in 30% alcohol	
2	M/5	M/20	5 0 c.c.	4.65 c c	4 5	4.35 in 10% alcohol	Ce K
					4 0	3 85 in 20% alcohol	$[Fe(CN)_6]$
					3 5	3 50 in 30% alcohol	
3	M/15	M/50	6 0 c.c	5 00 c c	5 40	5.25 in 10% alcohol	Ce K
					4 80	4.70 in 20% alcohol	$[Fe(CN)_6]$
					4 20	4 10 in 30% alcohol	
4	M/40	M/100	8 0 c.c.	7 00 c c	7 20	6 90 in 10% alcohol	Ce K
					6 40	6 30 in 20% alcohol	$[Fe(CN)_6]$
					5.60	5 60 in 30% alcohol	

DISCUSSION

From the above summary of observations in table XVII it will be clear that the potentiometric titrations give only one point of equivalence in support of the formation of the compound Ce K $[Fe(CN)_6]$ where the molecular ratio of the reactants $[K_4Fe(CN)_6]$ and $Ce(NO_3)_3]$ is as 1 1 It is further to be noted that the points of equivalence in aqueous medium are slightly lower than the theoretical values required for the formation of the above compound Kolthoff and Furman (loc cit) and Muller and Takagami (Z anal. Chem 1028 73 234) also observed that in precipitation reactions the maximum leap did not occur at the theoretical point of equivalence This discrepancy between the theoretical and the observed titre values may be due to the adsorption of Ce^{+++} ions by the precipitated complex which would tend to lower the titre values

My views on adsorption of Ce ions by the precipitate are supported by the titre values in presence of alcohol It will be seen from table XVII that in presence of increasing amounts of alcohol the observed titre values gradually go up to approach the theoretical titre values because alcohol helps to suppress the adsorption In presence of 30% alcohol the potentiometric titration curve has a regular shape and the theoretical and the observed titre values almost coincide

The potentiometric observations are in conformity with the conductometric results communicated in the previous paper

Note :—My grateful thanks are due to Dr A. K. Bhattacharya of Agra College, Agra for his valuable suggestion and guidance.

14

RHEOCHOR
PART I
(A Critical Review)

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Chemists have for long sought, but with indifferent success som expression that would co-relate the composition and structure of a liquid with its viscosity

Dunston and Thol [1] showed that in certain homologous series, a linea relation holds between the m lar weight, M, and log n at constant temperature wh n n is th viscosity They evaluated several atomic group and structural constants but the val e of these is severely restricted. Because ny selected temperature can only be within the range of liquidity of a relativ ly small number of substances. Linke using Sheppards equation

$$\log n = A + \frac{B}{T}$$

showed that constants A and B vary linearly with the number of carbon atoms in the homologus series, but this again is too restricted to be of general use

What was really needed therefore was som f ction of viscosity that is practically independent of th temperature ove a considerable range In a series f papers Herz[4] showed th t $\frac{Mn}{D}$ is a constant for non-associated liquids over such a range D being the liquid density

That a connection hould exist between viscosity and surface tension has long been realized. Sharma pointed out that log θ θ being th surface tension is in certain cases a linear function of log n over a restricted range of temperature A neat expression was obtained by Silverman and Roseveare who combined Macleod s equation with earlier one of Batschinki[1] and btained $\theta^{-1} = A/n + B$ where A and B are constant,

Friend[9] pointed out that over a considerable range of temperature from just below the boiling point downwards, $\theta/n^{\frac{1}{4}}$ is a constant for non-associated substances thus expressing viscosities in millipoises, he obtained

$$K = \theta/(10^3 n)^{\frac{1}{4}}$$

Tempo.	10°c.	20°c.	40 c	60°c	80°c
Benzene	11 0	11 4	11 9	12 0	11.8
Methyl Butyrate	10.2	10 4	10 7	10 7	10.5
Bromine	13.0	13.2	13.3	13.2	—

The value of K varies considerably with the nature of the substances so that K is by no means a universal constant. Hence for a given liquid K will remain constant only over a temperature range in which the structure remains substantially the same

Sugden[10] in 1924 showed that, $M\theta^{\frac{1}{4}}/D$ which he named the Parachor is an additive quantity independent of temperature Friend replaced $\theta^{\frac{1}{4}}$ by $n^{1/4}$ and showed that the quantity $Mn^{1/4}/D$ is independent of temperature over the range for which K is constant. He named this constant as Rheochor

With all liquids R rises as the melting point is approached. This is probably due to the grouping or orientation of the molecules which occurs prior to the solidification. On the otherhand, R again rises with the temperature from the boiling point upwards. At these temperatures, the vapour density 'd becomes appreciable and replacement of D by D+2 d gives a constant value for R over a greater temperature range

Thus by using the relation $R = \frac{M(10^3 n)^{1/4}}{D+2d}$

he obtained the following results.—

	100°c.	140 c.	180°c
)	109.5	109 8	109.2
Chl(	[illegible]	130.1	130.6
C(B	[illegible]	[illegible]	1.4.2
			—

For associated liquids e.g. alcohols R falls with rise of temperature, for such substances boiling point is a convenient temperature for comparison of R. It was further found that R is additive and anologous isomeride yield similar values. Isomeride of different types however yield some what different values. For monomeric substances, increase of external pressure appears to h ve only a slight effect on R. It was further observed that for monomerics R is a definite fraction of the molar critical volume Vc. Thus

	R	Vc	R/Vc
Benzene	110.4	257.0	0.428
Chloro Benzene	130.0	307.9	0.422
Chloroform	99.5	231.4	0.430
Ethyl Acetate	118.5	286.0	0.414
		Mean =	0.424

Friend and Hargreaves[11] extended their work and determined Atomic group and structural Rheochors at the boiling point. The work of Friend nd Hargreaves as regards the atomic structural and group Rheochors is summarized in the table below

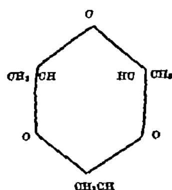
Atomic and Group Rheochor

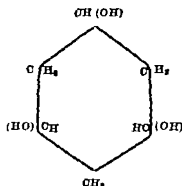
O	12.8	O=(Ketonic)	13.2
O<(Etheric)	10.0	CO-Valent Bond	0.0
H (in ordinary C–H)	5.5	CO-ordinate bond	0.4
H (in O–OH)	10.0	Cl	27.3
H (in HCl)	9.7	Br	35.8
H (in HBr)	L..6	I	47.6
H (in HI)	15.0	N (–)	6.6

CH_2 ....23.8

O H	(attached to alkyl radicals)	100.7
CO O	(Acids and Esters)	36.0
NH		20.6
NH		13.6
CN		33.0
	Saturated Sixmembered ring	–5.6

The use of Rheochor in solving structural problems is of importance. In case of paraldehyde for example, as mentioned by Glasstone [11] the parachor using Sugden's data, does not enable a decision to be made between the two possible cyclic formula.





I II

The observed rheochor of paraldehyde is 172.0 that of acetaldehyde is 62.4 According to formula (I) the difference between paraldehyde and three molecules of cetaldehyde consists in the removal of three ketonic double bonds and formation of a saturated six membered ring Hence the heochor of paraldehyde should be $3 \times 62.4 - 3 \times 3.2 - 5.6 = 172.0$ For formula II rheochor is 185.5 so the evidence is strongly in favour of formula (I)

Work on rheochor has also been done by some other workers Srivastava[12] studied the variation of rheochor with temperature. He calculated the rheochor values for a number of organic liquids With normal liquids (e.g with hydrocarbons and esters) the rheochor R showed a slight tendency to decrease first and then increase as the boiling point was approached. The total variation from the mean was $\ngtr$ 0.5%. In the case of associated liquids (e g. water and alcohol) R decreases with the rise of temperature and the variation from th mean is greater

Nayer and Srivastava[14] used rheochor values for the study of the constitution of iodic acid They drew graphs of rheochor (also parachor nd molecular refraction) against concentration of aqueous HIO_3, which showed discontinuities at 0.1N and 0.04N

They therefore, suggested that in concentrated solutions (HIO) is the dominant form and that this changes to diamer at concen trations < 0 01 Below 0 04N the monomer exists mainly in the ionized state. Th y also postulated, the electronic structures of these forms.

Nayer and Pande[13] tried to study the f rmation of complex compounds betwee lead nitrate and alkali nitrates (Th system $Pb(NO\ )_2$ –NH NO_3 –H O was studied.) A solution containing a constant amount of NH NO_3 and increasing amount of Pb (NO $)_2$ were ex mined with respect to rheochor viscosity parachor and some other properties. Each of these properties when plotted ag inst concentration showed three distinct breaks which accord ing to them correspond to the compounds Pb (NO $)_2$n NH_4 NO where n 1 2 and 4 and th t they system resembled that of Pb (NO_3) –KNO –H_2O rather than Pb $(NO_3)_2$ –Na NO –H O

Bhagwat and Tos iwal ad anced the view that rheochor like parachor can be determined by the solution method, both for liquids and solids by the expression

$$Rm = R (1-x) + xRx$$

Where Rm is the rheochor of the solution, R, th rheochor of the solv nt, Rx the rheochor f th solute and x and (1–x) the molecular fractio of th solute and the solvent respectively From the results given in the year book of 1937 th y showed the applicability of the law to sugar solution. Bhagwat and Mandlol[1] ext nded th work. Systematic work on this problem was carried out by Subnis and th d tails of the work are given in the next paper

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RHEOCHOR

PART II

(Application of Hammick and Andrews Equation to Binary Mixtures)

By

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Bhagwat and Toshniwal[1] suggested that like parachor rheochor can be determined by the solution method, both in case of solids as well as the liquids by th expression

$$R_m = R(1-x) + xR_x$$

where R_m is th rheochor of the solutions R the rheochor of the solvent and R_x that of the solute whose molecular fraction x is dissolved in $(1-x)$ fraction of the solvent.

R_m is given by the expression

$$R_m = \frac{M_m n^{1/8}}{D_m}$$

where M_m = mean molecular weight of the solution

n = viscosity

D_m = density of the solution

M_m is obtained from th relation

$$M_m = M(1-x) + xM$$

M and M being the molecular weights of the solvent and th solute respectively

From the results of n and D available from ch mist yearbook of 1937 they tried the applicability of the law to the ugar solutions. Bhagwat and Mandloi[2] extended the work but no systematic work was done. H nce to test the applicability of th law more extensive work was carried out by us Hammi k and Andrews[3] in their original work on th application of the mixture law to the parachors of liquids divided th liquid mixtures in th following groups (1) non-associated solutes in associated solvents (2) associated solutes in associated solvents, (3) associated solutes in non-associated solvents. We have carried out the work on similar lines at various temperatures and in general found that th mixture law is applicable in most of the cases.

Newton and Friend[4] in their original work, give the value of rheochor at the boiling points, since the values are constant only at that temperature Our work is carried out at lower temperatures and as such our values do not coincide with the theoritical values However as we are more concerned with the application of the mixture law and not the absolute rheochor values we have only seen the agreement between the experimental rheochor value of the pure liquid at a particular temperature and its rheochor value at the same temperature calculated from the mixture law

EXPERIMENTAL

Viscosity of the liquids and the solutions was determined with the help of Ostwalds Viscometer The same Viscometer and the same volume of the liquid was always used. A stopwatch was used to note the time of the fall of the fluid between the two marks. The temperature was maintained constant between the limits of $\pm 0{\cdot}1$ by immersing the viscometer as well as the pyknometer (used for determination of density) in a thermostat Substances used were A. R B D H. or Merck samples and the liquids were *distilled before the use*

If n_1 and n_2 be the viscosity of the solution and the water respectively d_1 d_2 their densities and t_1 and t_2 the time of fall then

$$\frac{n_2}{n_1}=\frac{d_2 t_2}{d_1 t_1}$$

The viscosity and density of water at the temperature of the experiment, was obtained from standard tables and the value n (the viscosity of the solution) was calculated. As the viscosity n is found to be very small the value $n \times 10^8$ is used during the calculations.

The rheochor of the solution is then calculated by the expression

$$R_m=\frac{M_m\,(n \times 10^8)^{1/8}}{D_m}$$

while that of the liquid by the equation

$$R=\frac{M\,(n \times 10^8)^{1/8}}{D}$$

where R_m and R are the rheochors of the solution and the pure liquid (solvent) M_m and M the mean molecular weights of the solution and of the pure liquid and D_m and D are their densities respectively

R_s the rheochor of the solute is calculated by the relation already explained viz. $R_m=(1-x)\,R+xR$

Extensive work was done as regards the application of the law but only few representative cases are tabulated here

LIQUID LIQUID MIXTURES

Rhecohor of Acetic Acid (in Benzene)

TABLE 1 (Temp 20°c)

x	D_m	$n \times 10^3$	M_m	R_m	R_x
0.0000	0.8782	6.79	78.00	112.8	—
0.2158	0.8964	6.58	74.10	104.5	75.1
0.3643	0.9140	6.84	71.43	99.5	76.2
0.4322	0.9210	6.70	70.73	97.4	76.5
0.5213	0.9340	6.84	68.60	93.4	77.0
0.7321	0.9520	7.23	64.82	87.2	77.8
0.9233	0.9731	8.08	61.37	81.9	79.1
1.0000	1.0465	11.03	60.00	—	78.8
					Mean=76.9

TABLE 2 (Temp 25°c)

x	D_m	$n \times 10^3$	M_m	R_m	R_x
0.0000	0.8746	6.42	78.00	112.6	—
0.2158	0.8944	6.32	74.10	104.3	74.5
0.3643	0.9100	6.61	71.43	99.4	75.6
0.4322	0.9191	6.50	70.73	97.2	76.1
0.5213	0.9312	6.63	68.60	93.3	76.3
0.7321	0.9480	6.68	64.82	86.7	77.2
0.9233	0.9681	7.16	61.37	81.1	78.5
1.0000	1.0432	10.98	60.00	—	78.0
					Mean=76.4

TABLE 3 (Temp. 30°c.)

x	D_m	$n \times 10^3$	M_m	R_m	R_x
0.0000	0.8708	5.99	78.00	112.0	—
0.2158	0.8904	6.10	74.10	103.9	74.1
0.3643	0.9072	6.28	71.43	99.1	75.3
0.4322	0.9152	6.24	70.73	97.1	75.5
0.5213	0.9279	6.42	68.60	93.2	76.1
0.7321	0.9430	6.53	64.82	85.9	76.4
0.9233	0.9632	7.10	61.37	80.0	77.3
1.0000	1.0432	10.55	60.00	—	77.3
					Mean=75.8

Rheochor of Benzene (in Methyl Alcohol)

TABLE 1 (Temp 30°c)

x	D	x 10^3	M_m	R_m	R_x
0,0000	0 7903	5 60	32.00	50 3	—
0 1598	0.8127	5 64	39 38	60 2	111.8
0 3449	0.8307	5.63	47 87	72.6	111 5
0 4474	0.8420	5 59	53 36	78.5	111 2
0 7425	0 8551	5 46	66.16	95 7	111 4
0 8277	0 8606	5 40	70 08	100 8	111 3
1 0000	0.8646	5.70	78.00	—	112.0
					Mean=111 4

TABLE 2 (Temp 40 c)

x	D	x 10^3	M_m	R_m	R
0 0000	0.7823	4 90	32.00	50 0	—
0 1598	0 8037	4 91	39.38	59 8	110 3
0 3449	0.8219	5.07	47 87	71 1	110 7
0 4474	0.8321	4 78	53.36	78 0	109 9
0 7425	0 8468	4 69	66.16	94 8	110 4
0 8277	0.8534	4 90	70 08	100 2	110 6
1 0000	0.8537	4 90	78.00	—	111.4
					Mean=110 4

TABLE 3 (Temp 50°c)

	D	n 10^3	M_m	R_m	R_x
0.0000	0 7747	4 16	32.00	49 7	—
0.1598	0.7971	4 11	39 38	58.8	109 0
0.3449	0.8131	4.05	47 87	70 3	109 3
0 4474	0.8238	4 14	53 36	77 4	109 6
0.7425	0.8385	4 11	66 16	94.0	109.6
0.8277	0.8420	4 13	70.08	96 4	109 8
1.0000	0.8447	4 15	78.00	—	106.2
					Mean=109 4

SOLID LIQUID MIXTURES

Rheochor of Urea (in water)

TABLE 1 (Temp 30 c)

x	D	η x 10³	M_m	R_m	R_x
0 0219	1 0210	9 35	18 92	24 6	54.3
0 0085	1 0400	8.72	20 02	25 5	60.9
0.0994	1 0760	9 91	22.15	27 5	63.8
0 1318	1 0960	10 87	23 54	28 9	65 2

Mean=61.2

Calculated value for th rheochor of Urea=64.0

Rheochor of Urea (in ethyl alcohol)

TABLE 2 (Temp 30°c)

x	D	10³	M_m	R_m	R_x
0 0258	0 8125	9 10	46.37	75 2	64 6
0 0362	0.8199	10.86	46.51	76.4	64 2
0.0583	0.8287	10.09	46 82	75.1	65.8
0 0721	0 8354	9 75	47.02	74 9	64 3

Mean=64 7

Rheochor of Acetamide (in water)

TABLE 3 (Temp 30°c)

x	D	η 10³	M_m	R_m	R
0 0363	1.0070	11 49	19 49	26.3	89 2
0 0438	1 0090	10.15	19.80	26.2	86 0
0.0791	1 0160	11 78	21 25	28.5	87 0
0.0928	1 0230	14 16	23 27	31 7	87.5

Mean=87 4

Calculated valu fo the rheochor of Acetamide=72.7

Rheochor of Achetamide (in ethyl alcohol)

TABLE 4 (Temp. 30°c)

x	D	η x 10³	M_m	R_m	R_x
0.0327	0.8083	9 42	46.42	76.1	84 6
0.0646	0 8175	10 00	46 75	76.3	84 3
0 0901	0.8236	10.16	47 18	76.5	84.8
0 1041	0 8275	12.61	47.37	76.8	86 2

Mean=84 9

DISCUSSION

The value R_x shows that the mixture law is applicable very satisfactorily in the case of liquid liquid mixtures. In case of acetic acid as well as in case of benzene the rheochor values obtained from the mixture law are to some extent lower than the actual values of the pure liquids. The calculated rheochor values of acetic acid and benzene are 76.9 and 111 4 respectively while the values for the pure liquids are 78 8 and 11_0 respectively which are fairly in agreement with the calculated values. In case of acetic acid the values at low concentrations are quite low but approach the value of the pure liquid as the concentration of acetic acid in the mixture increases

In case of solid mixtures the rheochor value of urea and acetamide is determined using two solvents viz. Water and ethyl alcohol As is clear from the tables the values seem to be more constant and approach the calculated value when ethylalcohol is used as a solvent rather than when water is used as a solvent. The calculated value of the rheochor of urea is 64.0 while the experi mental value in case of water is 61.2 and ethyl alcohol it is 64 7 The value in case of ethyl alcohol is clearly more satisfactory In case of acetamide the mean value in case of water and ethyl alcohol is 87 4 and 84 9 respectively and as such is much higher th n the calculated value which is 72.7 The mixture law thus seems to be more applicable in case of liquid liquid mixtures rather than solid liquid mixtures. Moreover as is clear from the tables the values of R_x in case of solids at different concentrations are not regular as is the case with liquids.

More work as regards the causes of this deviation is in progress. It is not unlikely that the deviation from the mixture law for the solutions of solids may be due to the fact that, the rheochor of the solid as obtained from the mixture law cannot be compared with the theoretical rheochor values, supposed to be the values at the boiling point of the substances. The validity of the mixture law in liquid solutions is clear since the rheochor of the liquid in pure state and that from the mixture law refer to the same temperature

In the third part of this paper an attempt has been made to test the applicability of the mixture law to ternary mixtures.

In case of the ternary mixtures the rheochor of the solution is given by

$$R_m = 1-x-y)\, R + x\, R\ + yR_y$$

SUMMARY

Mixture law has been tried to find the rheochor values of solids and liquids in case of binary mixtures. In case of liquids rheochor of acetic acid and benzene have been determined and *found to be fairly in agreement with th v lues of the pure liquids.* In case of solid liquids mixtures, the value of urea obtained is nearly the same as the theoretical value, the value of acetamide obtained is however considerably high when compared with th theoretical value. The mixture law thus seems to be more appli cable in case of liquid liquid mixtures rather than in case of solid-liquid mixtures.

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RHEOCHOR
PART III
(Application of Hammick and Andrews Equation to Ternary Mixtures)

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Subnis and Bhagwat (J Indian Chem Soc 1931 28, 275) attempted to see how far mixture law is applicable to the *Rheochor of ternary mixtures* Th work has *now been extended* to various tern ry mixtures The systems chosen in this paper are all consisting of liquids associated and non-associated In order to be able to know the exact xtent of application law has been studied over the whole range of concentration that is from zero molar fraction to molar fraction equal to one Results therefore over the whole range have been submitted. This study over the whole range was necessary to plot a graph and see whether straight line mixture law is applicable in so the simpl mixture law was not applicable Rhecohor is known to approach the theoretical value in case of pure liquids as the temperature is increased The law therefore has been studied at different temperatures for the same mixture In case of a ternary mi ture the Rheochor of the solution R_m is given by

$$R_m = (1-x-y)\,R + xR + yR_y$$

where R R and R are the Rheochors of the solute and the two solvents respectively and x y and 1 - x y are their molar fractions. R_m is given by

$$R_m = \frac{M_m}{D} \eta^{1/}$$

where η is the viscosity of the solution whose density is D The mean molecular weight M_m of the solution is given by

$$M_m = (1-x-y)\,M + x\,M + y\,M_y$$

where M M and M are the molecular weights of the solute and the two solvents respectively The results are recorded below —

RHEOCHOR OF BENZENE

Benzene, Toluene Carbontetra Chloride System

TABLE 1 (Temp 35 c)

R (Toluene)=132.2 R (Carbon tetra chloride)=129 7

x	y	1-x-y	M_m	D_m	$n \ 10^3$	R_m	R_x
0 1385	0 7929	0 0688	94 34	0 9046	5 46	128 9	111.3
0.3567	0.5395	0 1040	93 48	0 9303	5.14	124 1	111 4
0.4377	0 2995	0.2629	102.20	1.0580	6.00	121 3	111 4
0 6573	0.1305	0.2121	95.97	1.0220	5 94	117.3	110.9
1.0000	0.0000	0.0000	78.00	0 8648	5 17	110 8	—
							Mean=111 2

TABLE 2 (Temp 45 c)

R (Toluene=131 9) R (Carbon tetra chloride)=128 9

x	y	1-x-y	M_m	D_m	$n \times 10^3$	R_m	R_x
0 1385	0 7929	0.0688	94 34	0.8976	4 72	127 8	108.6
0 3567	0.5395	0.1040	93 48	0.9249	4 88	123 2	109 8
0 4377	0 2995	0 2629	102 20	1 0420	5.36	121.0	109.8
0.6573	0 1305	0 2121	95.97	1.0120	5 28	116 7	110.3
1.0000	0.0000	0.0000	78.00	0.8580	4 68	110 2	—
							Mean=109 6

TABLE 3 (Temp 55°c)

(Toluene)=131.4 R (Carbon tetra chloride)=128.1

x	y	1 -y	M_m	D_m	$n \times 10^3$	R_m	R_x
0 1385	0.7929	0.0688	94 34	0.8923	4.58	127 7	108.4
0.3567	0.5395	0 1040	93 48	0.9798	4 77	122.5	107 2
0.4377	0.2995	0.2629	102.20	1.0340	5 16	120 9	109 1
0.6573	0.1305	0 2121	95.97	1.0050	5.06	116.2	109.6
1 0000	0.0000	0.0000	78.00	0.8527	4 49	109 7	—
							Mean=108 6

RHEOCHOR OF BENZENE

Benzene, Ethyl Alcohol, Methyl Alcohol system

TABLE 1 (Temp. 35 c)

R(Ethyl Alcohol)=75.4 R(Methyl Alcohol)=49 7

x	y	1-x y	M_m	D_m	n x 10	R_m	R_y
0.0560	0 1782	0.7656	37.06	0.8021	5 91	57 7	109 8
0.1342	0.3712	0.4944	43 37	0.8141	6.39	67 1	109 6
0.2889	0.3217	0.3897	49 82	0.8266	5 19	75 2	109 0
0 6227	0.1933	0 1840	63 55	0.8507	5.60	92.6	110.4
1.0000	0.0000	0.0300	78.00	0.8648	5.17	110 8	—
							Mean=109 7

TABLE 2 (Temp 45°c)

R(Ethyl Alcohol)=74 3 R(Methyl Alcohol)=48.6

x	y	1 x y	M_m	D_m	$n \times 10^2$	R_m	R_y
0.0560	0.1782	0.7656	37.07	0.7918	5.01	57 2	108.6
0.1342	0.3712	0 4944	43.37	0.8041	5.36	66.5	108.0
9.2889	0.3217	0 4771	49.82	0.8183	5 08	74 7	109.3
0 6227	0.1933	0 1840	63.55	0 8409	4.77	91.8	109 9
1.0000	0.0000	0.0000	78.00	0.8580	4.68	110 2	—
							Mean=108 9

TABLE 3 (Temp 55°c)

R (Ethyl Alcohol)=73.8 R (Methyl Alcohol)=47 9

x	y	1-x y	M_m	D_m	$n \times 10^2$	R_m	R_y
0.0560	0 1782	0.7655	37.07	0.7875	4 67	57.0	106.6
0.1342	0 3712	0 4944	43.37	0.7989	4 88	66.2	107 9
0.2889	0.3217	0.3897	49 82	0.8114	4.70	74 5	109.2
0.6227	0 1933	0.1840	63.55	0.8328	4 25	91.5	109.5
1.0000	0.0000	0.0000	78.00	0.8527	4 49	109.7	—
							Mean=108.3

RHEOCHOR OF BENZENE

Benzene Methyl Alcohol, Toluene System

TABLE 1 (Temp 35 c)

(R Methyl Alcohol)=49 7 R (Toluene)=132.3

x	y	(1 x y)	M_m	D_m	$n \times 10^3$	R_m	R_x
0.0514	0.7563	0.1923	45.88	0.8245	5 40	68 7	110.6
0.2283	0 5392	0.2324	56.43	0.8368	5 14	82.7	110.7
0.3595	0.3020	0.3385	68.84	0.8527	5 10	98.9	109.5
0.5843	0.1141	0.3016	76.98	0.8602	5.04	109.5	109.7
0.7025	0 1506	0 1467	75 10	0.8618	5.10	104 0	109 9
1 0000	0.0000	0.0000	78.00	0.8648	5 17	110.8	—
						Mean=110.1	

TABLE 2 (Temp. 45°c)

R (Methyl Alcohol)=48 6 R (Toluene)=131 9

x	y	(1 x-y)	M_m	D_m	$n \times 10^3$	R_m	R_x
0.0514	0.7563	0 1923	45 88	0.8136	4 70	68.4	109.6
0.2283	0.5392	0.2324	56.43	0.8299	4 53	82.4	110.3
0.3595	0.3020	0.3385	68.84	0.8422	4 43	98.4	108 7
0.5843	0.1141	0.3016	76.98	0.8500	4 42	109 1	109 3
0.7025	0.1506	0 1467	73.10	0.8511	4 44	103.7	109.6
1 0000	0.0000	0.0000	78.00	0.8580	4 68	110.2	
						Mean=109 5	

TABLE 3 (Temp 55°c)

R (Methyl Alcohol)=47 9 R (Toluene)=131 4

x	y	(1 x y)	M_m	D_m	$n \times 10^3$	R_m	R_x
0,0514	0,7563	0 1923	45.88	0.8046	4.31	65 4	108.6
0,2283	0.5392	0.2324	56.43	0.8213	4 30	82.1	109.3
0.3595	0.3020	0.3385	68.84	0.8368	4 21	96.4	109.0
0.5843	0.1141	0.3016	76.98	0.8453	4 32	109 1	109 4
0.7025	0.1506	0 1467	73 10	0.8455	4 29	103.5	109 5
1 0000	0.0000	0.0000	78.00	0.8527	4 49	109 7	—
						Mean=109	

RHEOCHOR OF BENZENE

Benzene, Ethyl Alcohol, Toluene System

TABLE 1 (Temp 35 c)

R (Ethyl Alcohol) = 75 4 R (Toluene) = 132.3

x	y	(1 − y)	M_m	D_m	$n \times 10^3$	R_m	R_x
0.0768	0.7930	0 13 1	54 45	0.8247	7 86	85.4	110.0
0.1998	0.5790	0.2209	62.55	0.8358	6.31	94 2	111 4
0.3444	0 2768	0 3794	74.50	0.8531	5 75	108.7	110 1
0.6572	0.2524	0.0905	71 20	0.8549	5.60	130.3	110.1
1.0000	0.0000	0.0000	78.00	0.8648	5 17	110.8	—
							Mean = 110.4

TABLE 2 (Temp 45 c)

R (Ethyl Alcohol) = 74.3 R (Toluene) = 131 9

x	y	(1 x y)	M_m	D_m	$n \times 10^3$	R_m	R_x
0.0768	0 7930	0 1301	54 45	0.8172	6.40	84.0	108.4
0 1359	0.1489	0 7114	83 24	0.8437	4.56	119 1	107 6
0 3444	0.2768	0.3794	74.50	0.8422	4.89	107 9	109.3
0.6572	0.2524	0.0905	71.20	0.8441	4 79	102.6	109 7
1.0000	0.0000	0.0000	78.00	0.8580	3.68	110.2	—
							Mean = 109 0

TABLE 3 (Temp 55 c)

R (Ethyl Alcohol) = 73.8 R (Toluene) = 131 4

x	y	(1-x-y)	M_m	D_m	$n \times 10^3$	R_m	R
0.0768	0.7930	0 1301	54 45	0.8110	5 31	83.3	107 8
0 1998	0.5790	0.2209	62.55	0.8196	4 78	92.7	107 2
0.3444	0.2768	0.3794	74.50	0.8356	4 43	107 4	108.3
0.6572	0 2524	0.0905	71 20	0.8377	4 35	102 1	109 1
1.0000	0 0000	0.0000	78.00	0.8527	4 49	109.7	—
							Mean = 108.1

RHEOCHOR OF ETHYL ALCOHOL

Ethyl Alcohol, Methyl Alcohol & Acetone System

TABLE 1 (Temp 35 c)

R (Methyl Alcohol) =49 7 R (Acetone) =[illegible]

x	y	(1-x-y)	M_m	D_m	$\eta \times 10^3$	R_m	R_x
0.0834	0.8395	0 0771	35 16	0.7916	5.25	[illegible]	72.3
0 2252	0.0905	0.6842	52.94	0 7960	5.54	[illegible]	[illegible]
0.3634	0.3779	0.2586	43 81	0.7968	5.75	[illegible]	74.8
0.6386	0 1289	0.2328	47 01	0 7997	6.50	74.3	74 9
1 0000	0 0000	0 0000	46 00	0.8000	8.5[illegible]	[illegible]	—

Mean=74 4

TABLE 2 (Temp. 35 c)

R (Methyl Alcohol) =48 6 R (Acetone) =86.7

x	y	(1-x-y)	M_m	D_m	$\eta \times 10^3$	R_m	R_x
0.0834	0.8395	0.0771	35 16	0.7832	4.64	54 4	71.5
0.2541	0.5048	0.2413	41 83	0.7674	4.82	64 7	73.5
0.3634	0 3779	0.2586	43.81	0.7905	4.98	67.7	73.0
0.6386	0 1289	0.2328	47 01	0.7921	5.35	73.2	73.4
1.0000	0.0000	0.0000	46 00	0.7964	7 23	73.9	—

Mean =73.4

TABLE 3 (Temp 55 c)

R (Methyl Alcohol) =47.9 R (Acetone) =[illegible]

x	y	(1-x-y)	M_m	D_m	$\eta \times 10^3$	R_m	R_x
0.0834	0.8395	0.0771	35 16	0.7784	4.29	54.2	69.5
0 2252	0 0905	0.6842	52.94	0 7820	3.79	79 9	73.1
0.3634	0.3779	0. 586	43.81	0.7814	4.40	67 4	72.1
0.6386	0 1289	0.2328	47.01	0.7857	4 88	72.9	72.8
1.0000	0.0000	0.0000	46.00	0 7918	6.32	73.2	—

Mean=71 9

RHEOCHOR OF ETHYL ALCOHOL

Ethyl Alcohol, Benzene & Methyl Alcohol System

TABLE 1 (Temp 35 c.)

R (Benzene)=110 8 R (Methyl Alcohol)=49 7

x	y	(1 x y)	M_m	D_m	n 10^3	R_m	R_x
0.1489	0 1359	0 7114	83.24	0.8521	5 20	120.0	73 7
0.2768	0 3444	0.3794	74.50	0.8531	5 75	108.7	74 4
0.5790	0.1998	0 2209	62.55	0.8358	6 31	94 2	74.3
0.7930	0.0768	0.1301	54 45	0 8247	7.86	85 4	75 4
1 0000	0 0000	0.0000	46.00	0.8001	8.80	75 6	—
							Mean=74 2

TABLE 3 (Temp 45 c.)

R (Benzene)=110 2 R (Toluene)=131 8

x	y	(1 x y)	M_m	D_m	n x 10^3	R_m	R_x
0.1489	0.1359	0.7114	83.24	0.8437	4.50	119 1	71 3
0.2768	0.3444	0.3794	74.50	0.8422	4.59	107 9	73 1
0.5790	0.1998	0.2209	62.55	0.8260	5 44	93 6	73.5
0.7930	0.0768	0.1301	54 45	0.8172	6.40	84 0	73 8
1.0000	0.0000	0.0000	46.00	0.7964	7.23	73 9	—
							Mean=72 8

TABLE 3 (Temp 55 c.)

R (Benzene)=109 7 R (Toluene) 131 4

	y	(1 y)	M_m	D_m	n x 10^3	R_m	R
0.1489	0.1359	0.7114	83 24	0.8371	4.31	119 1	69.8
0.2768	0 3444	0.3794	74.50	0.8356	4 43	107 4	72.1
0.5790	0.1998	0 2209	62.55	0.8196	4 78	92.7	72 3
0.7930	0.0768	0.1301	54 45	0.8110	5 31	83.3	73.3
1.0000	0.0000	0.0000	46.00	0 7918	6.32	73.1	—
							Mean=71.9

RHEOCHOR OF ETHYL ALCOHOL

Ethyl Alcohol, Benzene & Methyl Alcohol System

TABLE 1 (Temp 35 c)

R (Benzene)=110 8 R (Methyl Alcohol)=49 7

x	y	(1-x-y)	M_m	D_m	$\eta \times 10^3$	R_m	R_x
0 1782	0.0560	0 7656	37.07	0.8021	5.91	57 7	74.6
0.2856	0.2172	0 4771	46.90	0.8243	5.81	71 1	73 4
0.3713	0.1342	0.4944	43.37	0.8141	6.39	67 2	74.2
0.5989	0 0682	0 3328	43.51	0.8087	7 29	68.9	74.6
1.0000	0.0000	0.0000	46.00	0.8001	8.80	75.6	—

Mean=74.2

TABLE 2 (Temp 45 c.)

R (Benzene)=110.2 R (Methyl Alcohol)=48.6

x	y	(1 x-y)	M_m	D_m	$\eta \times 10^3$	R_m	Rx
0 1782	0.0560	0.7656	37.07	0.7918	5.01	57 3	73.2
0.2856	0.2372	0.4771	46.90	0.8102	4 97	70.6	72.7
0.3713	0 1342	0.4944	43.37	0.8041	5.36	66.5	73.1
0.5989	0.0682	0.3328	43.51	0.7979	5.93	68 1	73.6
1.0000	0.0000	0.0000	46.00	0.7964	7 23	73 9	—

Mean=73 1

TABLE 3 (Temp. 55 c.)

R (Benzene)=109.2 R (Methyl Alcohol)=47.9

x	y	(1-x-y)	M_m	D_m	$\eta \times 10^3$	R_m	R_x
0.1782	0.0560	0.7656	37.07	0 7875	4.67	57.0	72.3
0.2856	0.2372	0.4771	46.90	0.8078	4.35	69.6	69 9
0 3713	0.1342	0.4944	43.37	0.7989	4.88	66.2	72.5
0.5989	0.0682	0.3328	43.51	0.7939	5 48	67.8	73 1
1.0000	0.0000	0.0000	46.00	0.7918	6.32	73.1	—

Mean=71.9

Rheochor of Benzene was dertermined in Ternary Systems consisting of Toluene and carbon tetrachloride Ethyl alcohol and methyl alcohol toluene and ethyl alcohol and methyl-alcohol and toluene In all cases the mixture law seems to be applicable over the entire range of molar fraction of Benzene The value of pure liquid as observed is 110 8. The values obtained in mixture are practically the same. At low molar fraction a slight variation is observed which may be due to experimental error since as the value of x falls the error is multiplied much more in calculating Rx The temperature variation does not seem to have appreciable influence on the Rheochor value although the value falls slightly with temperature.

Rheochor of Ethyl alcohol was investigated in Ternary Systems consisting of Benzene and Toluene methyl alcohol and benzene and in methyl alcohol and acetone Here again the mixture law seems to be applicable at all temperatures and for all molar fractions extending from zero to one. The value for pure liquid which is 75.6 agrees with the value calculated from ternary mitures. As in case of Benzene the values show slight deviation at lower molár fractións.

My thanks are due to Dr W V Bhagwat for his interest throughout the work.

SUMMARY

Mixture law is found to be applicable to ternary mixtures over the entire range of molar concentration. Systems investi gated were

(1) Benzene in Toluene and carbon tetrachloride Ethyl alcohol and methylalcohol Toluene and ethylalcohol Methylalcohol and toluene

(2) Ethylalcohol in Benzene and toluene Methylalcohol and Benzene and Methylalcohol and acetone

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DIAMAGNETIC ANISOTROPY IN RELATION TO CRYSTAL STRUCTURE

(Chlorates and Bromates)

By

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[Abstract: Principal diamagnetic susceptibilities of chlorate bromate ions in crystals have been measured nd correlated with their known structure]

INTRODUCTION

In a recent paper the author (Mookherji 1931 correlated the principal diamagnetic susceptibilities of some bicarbonates and nitrates with their known fine structure It was found that for CO_3 or NO_3 groups which are planar K_{II} susceptibility normal to the plane of CO or NO group is greater than K that in the plane algebraically and that $K_1 - K_{II} = 5.0 \times 10^{-6}$ for CO group and 5 4 $\times$ 10^{-6} for NO groups. Ranganadhan (1929) observed that the magnetic birefringence in solutions f carbonates and nitrates is positive This positive ign indicates that for approximately uniaxial crystals the direction of maxim m diamagnetic susceptibility is one of least refractive index. Chinchalkar (193*) as a result f measurement of magnetic birefringence of chlorate and bromate ions in aqueous solution came to the conclusion th t the sign of birefringence in ClO and BrO ions is negative, which hows that for ions like ClO and BrO the maximum diam gnetic usceptibility must correspond in direction with maximum refrac tive index. In other words K_{II} should be algebraically sm ller than K for ClO_3 and BrO_3 ions. Magnetic anisotropy measurements of single crystals of KClO by Krishnan G ha and Ba erji (1933) do reveal such a res lt This difference in beh viour of ClO and BrO_3 ions with that of NO_3 and CO_3 ions is very striking and it would be very interesting to study the directional

properties of chlorate and bromate ions with a view to obtain a knowledge about their principal susceptibilities which when correlated with their fine structure might provide an explanation of the difference in their magnetic behaviour

EXPERIMENTAL

Crystals were grown out of aqueous solution at room temperatures. Chemicals used were of Mercks analytical variety The d termination of magnetic anisotropy were carried out by the method of Krishnan and Banerji (1935) Absolute susceptibility in a convenient direction of the crystal was determined by the method as developed by Datta (1944). Liquids used for such measurements were carbon tetra-chloride and Nitrobenzene of *volume susceptibility* $-.684\times10^{-6}$ and $-.595\times10^{-6}$ respectively as given in International critical Tables Vol VI.

RESULTS

Results of measurements are collected in tables I and II and ar expressed in the usual units i e 10^{-6} of a C G S E M U For hexagonal crystal χ_{11} respresents the gram molecular susceptibility along the symmetry axis and χ_{1} that along directions normal to it In rhombic crystals χ_a χ_b and χ_c are the gram molecular susceptibility along a b and c crystallographic axes respectively For monoclinic crystals χ_3 is the gram molecular susceptibility along b axis while greater of the two in the symmetry plane (010) is denoted by χ_1 and the smaller by χ_2, θ is the angle which χ_2 axis makes with a-axis and ψ is that between χ_1 axis and C axis

χ denotes the mean of the three principal suscept ies and is given by $\frac{\chi_1+\chi_2+\chi_3}{3}$ for monoclinic crystals χ χ for rhombic crystals and $\chi_{11}+2\chi_{1}/_3$ for trigona is Pascal s additive values were from Stoner's book on Ma nd matter (1934) and Selwood s magnetochemistry (1943).

TABLE I
ANISOTROPY

Unit for X's is 10^{-6} of c.g.s. E M U

No.	Crystal.	Crystallographic data.	Mode of suspension.	Orientation in the field	$K \times 10^6$	Magnetic Anisotropy
1.	K ClO_3	Mond Prism C^2_{2h} Z=2 a=4,647 A b=5 585 c 7 085 β=109 38,,	b axis vertical 'a (001) pl horiz.	ϕ=−39 6 b axis normal to field ,,	5 41 3 40 2 45	$\chi_1-\chi_2$=5 41 $\chi-\chi_3$=5 66 θ=+50,2 cal $\Delta\chi$=2 45
2	$Ba(ClO_3)_2$ H_2O	Mond Prism C^b_{2h} Z=4 a=8,80 A b=7,80 ,, c=9,35 β 93,5	b axis vertical 'c axis b and 'c axis horizontal	$(\theta)_1$=+60° 0 b axis parl to field b axis	5,54 0 74 3,06	$\chi_1-\chi_2$=5,54 $\chi_1-\chi_3$=0,57 θ=+60 0 cal. $\Delta\chi$=3,06
3	$Sr(ClO_3)_2$	Rhombic a : b : c= 0 9174 1 : 1 6005	'a axis vertical b c	'c axis along field c ,, 'a	5 03 3 69 1,34	$\chi_a-\chi_b$=5,03 $\chi_c-\chi_a$=3,69 cal $\Delta\chi$=1,34
4	K BrO	Hexagonal 7=1 C^5_{3v}	Hexag axis horiz	Hexag axis along field	5 18	$\chi_{11}-\chi_1$=5 18

TABLE II

ABSOLUTE SUSCEPTIBILITY

Serial No.	Crystal	Direction along which sus. was measured.	Density of the crystal	Vol. susceptibility	Principal susceptibility	Mean susceptibility	
						Our Value	Pascals. Additive
1	$KClO_3$	along χ_1—axis	2 321	−0 853	$\chi_1 = -45\ 0$ $\chi_2 = -50\ 4$ $\chi_3 = -50\ 6$	−48 7	−45 1
2.	$Ba(ClO_3)_2H_2O$	„ b—axis	3.179	−1 014	$\chi = -102.3$ $\chi_2 = -107.8$ $\chi_3 = -102\ 9$	−104.3	−104.3
3	$Sr(ClO_3)_2$	„ a axis	3 151	−1 002	$\chi_a = -81\ 0$ $\chi_b = -82.3$ $\chi_c = -77.3$	−80.2	−84.9
4	$KBrO_3$	„ $\chi_{\parallel}$ axis	3.270	−1 075	$\chi_{\parallel} = -55\ 1$ $\chi_{\perp} = -60.2$	−58.5	−54 7

MAGNETIC ANISOTROPY IN RELATION TO CRYSTAL STRUCTURE

KClO —Its structure has been analysed by Zachariasen (1924) by X ray methods. H finds that there are two molecules in the unit cell and the ClO groups have pyramidal structure. Three oxygen molecules forming approximately an equilateral triangle at the three vertices and the chlorine atom at the centre of the oxygens being at a distance of 0 5A from th plan of the oxygen atoms *Plane containing oxygens are parallel to each other and* are parallel to b axis. The direction perpendicular to oxygen planes is the axis of approxim te uniaxial symmetry Let K_{11} represent gram molecular susceptibility along normal to the plane containing oxygen atoms and K that along directions in that plane

Hence K $= \chi_s$. From table I we find that $\chi_s - \chi_s = .25$ and hence the plane containing χ_s and b axis is the plane of symmetry i. e th plane containing oxygen atoms. Thus K_{11} normal to the plane is equal to χ_1 Hence

$$\chi_1 - \chi = K_{11} - K = 5\ 66$$

and $\chi_1 \quad \chi_s = K_{11} - K = 5\ 41$

therefore for ClO ions K K_{11} can be taken as 5.54, almost the same as nitrates and chlorates but with a negative sign.

Ba (ClO)$_2$ H_2O — It crystallises in the monoclinic system with four molecules in the unit cell. Referring to table I we find that $(\chi - \chi_s) + (\chi_1 - \chi$ (= 3 06 which is much smaller than $K_{11} - K$ = 5.54 for ClO ions. Hence all the eight ClO groups in the unit cell will not interest the (olo) plane in the same direction.

We find on referring to table II that χ — axis is an approximate axis of magnetic symmetry Let the normals to the planes of oxygen atoms of ClO group make an angle δ with this χ_s — axis.

$$\text{Evidently } K_{11} - K_1 = \frac{X_1 - X_1}{\frac{1}{2}\sin^2\delta - \cos^2\delta}$$

substituting the value of $\chi_1 - \chi$ = 2.77 and dopting K_{11} — K for ClO as 5 54 as obtained in KClO crystals we have $\delta = 63.°0$

Hence the normals to the molecular planes are inclined to X_2-axis at an angle of 63 0 degrees which is inclined to c axis at an angle of 29 °1 to 'a axis at an angle of 57 °3 and to b axis at an angle of 48 7

Recently the fine structure of Ba $(ClO)_2$ H_2O has been studied by X ray methods by Kartha (1952) It is assigned a space group C^6_{2h}. The ClO groups in the crystal retain their usual pyramidal form After a detailed analysis he finds that the normal to the plane containing the oxygen of ClO group makes an angle 49 3 degrees with b -axis nd is the same for all the ClO ions. This agrees very well with our value 48 7 degrees as deduced from magnetic date

Optically we should expect from the above magnetic orientations the two principal refractive indices α and β to be almost equal and smaller than γ which is supported by experiment (Groth 1908)

Sr $(ClO)_2$. It crystallises in the orthorlombic form

Let l m and n be the direction cosi es of the normal to the plane of oxygens of ClO ion. Then we have

$$l^2 - m^2 = \frac{\chi_a - \chi_b}{K - K}$$

$$l^2 - n^2 = \frac{\chi_a - \chi}{K - K}$$

and $l^2 + m^2 + n^2 = 1$

using the value of $\chi_a - \chi_b$ and $\chi - \chi_a$ from table I and taking $K_1 - K_1$ for ClO as 5.54 we find that K_{11} axis i e normal to the plane cont ining oxygens of ClO group makes an angle of 30 °0 degrees *with 'a axis 22°4 degrees with b axis and 50° 2 with* c axis Thus χ_b should be greater than χ and χ_c. χ should be the least This is what is observed as is given in table II. At present there is no X-ray data to verify the above molecular orientations.

KBrO It crystallises in the hexagonal system. Its structure has been studied by X-ray methods (Nature vol.113). It has one molecule in the unit cell The BrO group has got the same pyramidal form as the ClO group It is found that the planes the three oxygens of the BrO ion is perpendicular to the axis of

symmetry of the crystal. Hence using the same notations as in KCLO crystal we find that

$$X = K_{II} \text{ and } X = K_I$$

Thus $X_I - X_I = K_{II} - K_I = 5\ 18$ almost the same asymmetry as the CLO ions

COMPARISON MAGNETIC ANISOTROPY OF CHLORATE ION WITH THAT OF CARBONATE AND NITRATE IONS

CO and NO groups which are planar the susceptibility norm l to the plane of CO or NO group is greater than the suscept bility in the plane of the groups. This is attributed by Lonsdale (1939) to the existence of double bonds in NO and CO ions, which introduce a force constraining certain electrons to occupy plane orbits whose effective area is larger than the norm l ionic radius hence an abnormal diamagnetism normal to the plane f CO or NO results. For CO group the radius of this plane orbit is 1.05 A since $K - K_{II} = 5.4 \times 10^{-6}$ for CO group

In strong contrast to the magnetic behaviour of CO and NO ions is that of ClO and BrO ions. For in ClO and BrO ions K_I is greater than K_{II} Such cases have been observed by Lonsdale (1939) in aliphatic compounds, and is attributed to the absence of double bonds in aliphatic compounds.

The conventional electronic structure of chlorate ions ccording to Pauling (1934) shows that an unshared pair of electrons on th chlorine occupies one of its outer orbitals and the bond distances show a large amount of double bond character This view contradicts Lonsdale's explanation of K_I being greater than K when applied to ClO or BrO group Th t is to say since ClO ion also h ve double bonds K_{II} for them should be greate than K which is against experimental findings

VAN VLECK'S THEORY

According to V n Vleck (1934) polyatomic molecules with zero spin will have their entire orbital moment of the high frequency type unless the molecules have some unusual symmetry This

high frequency part will contribute to the magnetic moment of the molecule perpendicular to the resultant angular momentum. Then the susceptibility of such molecules is given by

$$X_{mol} = -\frac{Ne}{6\,me^2} \Sigma \bar{r}^2 + \frac{2}{3} N \Sigma \frac{m\;(n\;;n')}{h\lambda(l)(n';n)} \quad (I)$$

where m (n n) is an element of the electronic angular momentum matrix corresponding to the transition frequency ν (n n) all the other symbols have their usual significance

The first term of the above expression is the usual Pauli expression for diamagnetism. Because of the presence of the second term a polyatomic molecule of the above type m y be paramagnetic or diamagnetic

The direct evaluation of the sum over the excited states is difficult, hence $\lambda(l)$ (n n) is replaced by ν which is a sort of mean absorption frequency

THEORY APPLIED TO CO AND ClO_3 IONS.

According to equation (I) susceptibility for directions along the normal to the plane of the ions will be given by

$$K_{11} = \frac{Ne}{6\,mc^2} \Sigma r^2 + 2/3 \Sigma \frac{m_e\,(n\,n)}{h\nu_1}$$

where ν_{11} is the mean absorption frequency along the norm l to the plane of the molecule and for direction in the plane of the ion is given by

$$K_1 = \frac{Ne}{6\,mc^2} \Sigma r^2 + 2/3 \Sigma \frac{m_e\;(n\,n)}{h\nu_1\;(n.n)}$$

to where ν is the mean absorption frequency in the plane of the molecule so that the anisotropy of the molecule is given by

$$K_{11} - K_1 = 2/3 \Sigma \frac{m_e(n;n')}{h} \left\{ \frac{1}{\nu_{11}} - \frac{1}{\nu_1} \right\}$$

Thus the anisotropy $K_{11} - K_1$ will positive or negative depend ing on whether ν is greater or smaller than ν

For NO ions we find that $K_{11} - K_1$ is negative showing that ν_1 is greater than ν 1 Krishnan and Das Gupta ( ) have studied absorption spectra of Na NO and KNO crystals They find that ν_1 is greater than ν_{11} in NO ions.

In ClO and BrO ions K_{11} K_1 is positive hence it is expected that ν_{11} in these ions should be greater than ν_1 At present there is no directional bsorption data on these ions to verify ur conclusions

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18

DIAMAGNETISM OF TARTRATES IN STATE OF SOLUTION

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[Abstract : The susceptibilities of some tartrate have been measured in state of solution It is found that the change of susceptibility with concentration is a linear one within the change studied. The susceptibilities of dissolved substances were about 3% more than that of the solids]

INTRODUCTION

The effect of concentration on diamagnetism of solutions has been studied by many investigators It was found that for alkali halides the susceptibility varied linearly with concentration (Veiel 1935) With 1 to 90% aqueous solution of Sodium and Potassium nitrates the result is the same (Ranganadham and Qureshi 1940). Scott and Blair (1933 found that for aqueous solution of hydrochloric acid the relation is linear but the same is not true for Lithium-Chloride Trew and Spencer (1936) as a result of magnetic studies of several binary mixtures came to the conclusion that susceptibility χ of a mixture follows Wiedemann additive law $\chi = \chi_1 c_1 + \chi_2 C_2 + \ldots \chi_n C_n$ where...... (1) χ_1 C_1 etc. are the susceptibilities and weight fractions of the respective constituents of the mixture.

Inspite of all the above it is not safe to conclude that susceptibility and concentration is a linear relation. There are a good number of evidences of the deviation from the Wiedemann

additive law Fromic acid and water mixture (Rao and Narayanswami 1939) Aqueous solution of nitric acid (Ranganadham and Qureshi, 1935) are glaring examples

Hence it was thought worth while to study alkali tartrates in state of solution to reveal the influence of concentration on their diamagnetism

EXPERIMENTAL

Chemicals used were of Mercks reagent quality Double distilled water was used for making solutions.

Experimental arrangement adopted for the present measurements was the same as used in the measurement of powdered tartrates (Mittal 1953) Th differences of weights with magneti field on and off for different concentration were small hence the results so obtained by the above method were checked by a Datta balance (1944) where the angles of rotations could be measured more accurately The results obtained by both the methods agree well

RESULTS

Results of measurements are collected in tables 1 to 4.

C_s represents the concentration of the solution and is giv n by

$$C_s = \frac{\text{Weight of the substance dissolved.}}{\text{Total weight of the solution.}}$$

χ represents the susceptibility of the solution and is expressed in the usual units of 10^{-6} of a C G S E M.U ρ represents the density of the solution.

The nature of variation of susceptibility with concentration is shown in the graphs Figure 1 to 4.

TABLE I

Temp 22°C

Tartaric Acid

C_0	p	−X
0.50	2.0	0.5846
0.40	1.69	0.6302
0.33	1.50	0.6421
0.25	1.35	0.6520
0.20	1.28	0.6700
0.15	1.11	0.6985

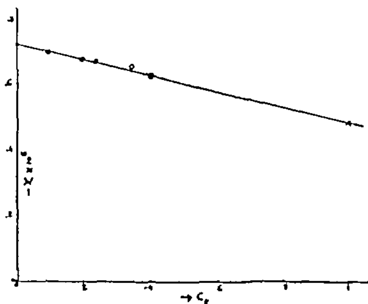


TABLE II

Temp. 22°C

Ammonium Tartrate

C_s	ρ	X
0.375	1.60	0.6400
0.333	1.50	0.6410
0.300	1.48	0.6485
0.250	1.40	0.6615
0.200	1.30	0.6801
0.150	1.15	0.6920

Fig No. II

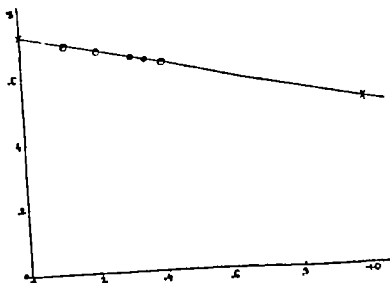


TABLE III

Tempr 22 C

Sodium Tartrate

C	P	X
0.370	1 58	0 6195
0.330	1.50	0 6200
0.280	1 4_	0 6291
0.230	1.35	0 6403
0.200	1 29	0 6010
0 150	1 13	0 6801

Fig N III

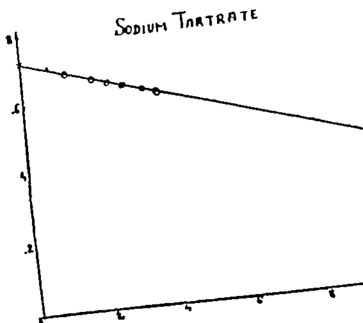


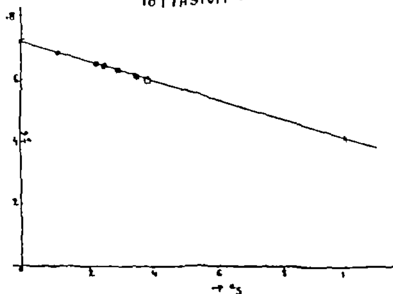
TABLE IV

Tempr 22 C

Potassium Tartrate

0	ρ	X
0.50	2.0	0.4852
0.40	1.65	0.5903
0.375	1.60	0.6000
0.333	1.48	0.6140
0.285	1.40	0.6343
0.250	1.35	0.6421
0.200	1.25	0.6610
0.150	1.10	0.6985

Fig No IV



INFLUENCE OF CONCENTRATION ON SUSCEPTIBILITY

The changes of susceptibility of Tartrates in state of solution with concentration for the salts studied by us follow a linear law with deviations not more than 1% in each case as shown in the graphs fig 1 to 4. The relations can be expressed

1 For Tartaric acid by

$$\chi = -.25\, C_s + 72 \qquad (2)$$

2. For Ammonium Tartrate by

$$\chi = -.22\, C + 72 \qquad (3)$$

3 For Sodium Tartrate by

$$\chi = -.20\, C_s + 72 \qquad (4)$$

and 4. For Potassium Tartrate by

$$\chi = -.21\, C_s + 72 \qquad (5)$$

From the above equations it is seen that the rates at which susceptibilities vary are different for diff rent salts. The rate is highest for Potassium and least is for Ammonium salt. In all cases the solvent is water so the rate of variation of susceptibility with concentration will depend on the susceptibility of the solute The smaller the susceptibility the greater will be rate of variation This view is supported by the result of susceptibility measurements on them. (Mittal 1953).

SUSCEPTIBILITIES OF TARTRATES AS SOLIDS AND IN SOLUTION

Few investigations had been made to determine how far the diamagnetism of ions or molecules are affected by the presence of neighbouring ions, by surrounding the solvent molecules in solutions. Hocart (1929) found that the susceptibility of alkali and alkaline earth halides in state of solution differs from those of the salts in the solid state The dissolved salts have susceptibilities some two to three percent higher than those for solids.

In equations 2 3 4 and 5 if C_s is put equal to zero we should get the value of susceptibility which should be that of water and actually we obtain $\chi = 72 \times 10^{-4}$ Thus the susceptibility of water when mixed with tartrates does not change Hence we can obtain the susceptibility of the dissolved substance from

the susceptibility of the solution by putting $C_s = 1$ (i e the dissolved solid), or by computating χ solid values by using formula 1 which takes the form $\chi_{so} = \chi_{solid} \times C_s + (1 - C_s) \times H_2O$ for two constituents.

The results so obtained are entered in table V below The susceptibilities for solid is from Mittal (1963)

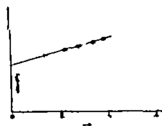
TABLE V

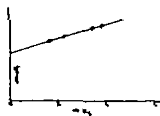
Substance	$\chi \times 10^{-6}$		Deviation ratio.
	Solid	Dissolved	
Tartaric acid	46	47	1·02
Ammonium Tartrate	·48	50	1·04
Sodium Tartrate	41	43	1 05
Potassium Tartrate	·40	41	1·02

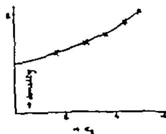
Figure V

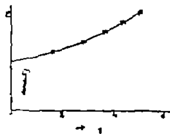
Amm nium Tartr te

Sodium Tartrate









Thus on the average the susceptibility of the dissolved tartrates are about three percent higher than the solid Salts

Diamagnetism of substances depends on the effective spread of the electron density distribution imposed by the surrounding ions or molecules

In solids and in dissolved salts the effective spread of the electron density distribution has a limitation. Hence diamagnetism of free molecules will be more than that of dissolved salts and solids, and hence dissolved salts will have more diamagnetism that the solid salts as found experimentally

The density of dissolved salts when plotted against concentration is not exactly linear in all cases as shown in the figure 5

ACKNOWLFDGEMENT

The work was carried out in the Physical Laboratories, Birla College of Science Pilani. The author wishes to thank Professor A. Mukherji, D Sc Head of the Dept of Physics for suggesting the problem and for his guidance and constant help Thanks are also due to Dr R. D Gupta, Head of the Dept of Chemistry for lending some instruments in connection with the work

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19

NUCLEAR EXCITATION AT HIGH TEMPERATURES

By

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[**Abstract :** The partition function of the nucleus C^{12} is calculated and the contributions to energy entropy and free energy due to the excitation of the nucleus derived.]

The stationary states of many of the atomic nuclei have been well established from a study of several nuclear reactions[1] They are generally few in number They may be expected to be thermally excited at sufficiently high temperatures and to be in a state of thermal equilibrium The excitation of a nucleus would contribute to the energy entropy and free energy of the system as distinct from such contributions from the translatory motion of nuclei The partition function of the nucleus C^{12} is calculated here and the other properties derived from it Taking the energy of the ground state as zero the energies of the excited levels is taken to be 4·47 7·0, 9·7 10·3, 10·8, 16·11 16·71 20·0 and 27·0 Mev[1] If Z is the partition function, the energy E, the entropy S and the free energy F are given by—

$$E = kT \frac{d(\log Z)}{dT}$$

$$S = k \log Z + kT \frac{d(\log Z)}{dT}$$

$$F = E - ST$$

TABLE I

T	$5\ 10^{[illegible]}$	$5 \cdot 10^{10}$	$5\ 10$	$5 \cdot 10^{11}$	$5 \cdot 10^{12}$ °C	
Z	1	1 78	7 56	9 71	9·97	10·0
$\frac{d(\log Z)}{dT}$	0	$1{\cdot}72 \times 10^{-11}$	$5{\cdot}23 \times 10^{-12}$	$5{\cdot}90 \times 10^{-13}$	$6{\cdot}00 \times 10^{-1[illegible]}$	
E	0	$5{\cdot}9 \times 10^{-6}$	$1\ 8 \times 10^{-5}$	$2\ 0 \times 10^{-4}$	$2{\cdot}00 \times 10^{-4}$	$2{\cdot}06 \times 10^{-4}$ erg
S	0	$1\ 90 \times 10^{-[illegible]}$	$3\ 14 \times 10^{-[illegible]}$	$3\ 16 \times 10^{-16}$	$3\ 12 \times 10^{-[illegible]}$	$3\ 156 \times 10^{-16}$ erg/°C
F	0	$1\ 1 \times 10^{-6}$	$1\ 4 \times 10^{-[illegible]}$	$1\ 58 \times 10^{-6}$	$1\ 56 \times 10^{-[illegible]}$	

The Table I shows calcul tions for som represent tive t mperatures The last column shows th limiting values attained beyond a certain temperature.

DISCUSSION

It can be seen that the contribution per excited nucleus to the ntropy energy and free energy is negligible for temperatures below about 10^{10} K There is a sudden rise between 5 10^{9} K nd 5 10^{11} K. A maximum is reached t 5 10^{11} K, and ultimately the energy and entropy settle down to constant limiting v lues.

The interest in the problem becomes naturally constrained firstly because it is scarcely probabl that such high tempera tures can at ll be attained in any material system, and secondly ev n if it could be so it is doubtful whether any nucleus can then remain stable. For example the energy of thermal agitation of the C^{12} nu leus at such high temperatures would far exceed the binding energy of th three alpha particles which can be assumed to constitute the nucleus. In any case the total contribution of such heavy nu l i would be small due to their much smaller concentration in comparison with hydrogen and heli m in stellar interiors The alculation has been carried out for C^{12} only as the behaviour of other nucl i could not be m h diff rent.

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INTERNAL PRESSURE IN A LIQUID

By

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[Abstract An equation is derived which makes it possible to calculate the internal pressure in a liquid Value of compressibility for water is calculated from the knowledge of the internal pressure and compared with the observed one. The equation can also be used to determine the factor n, which gives an indication of the size of the hole necessary for the viscous flow from the compressibility date of a liquid]

The problem of the determination of the internal pressure of a liquid is of great significance. Thus the influence of a solvent on the reaction velocity is dependent on its effect on the activity co-efficient and this is determined by the molar volumes and the internal pressure terms. Since the molar volumes generally do not vary greatly the specific rate constant is determined to a greater extent, by the difference between the internal pressure of the solvent and the internal pressures of the reactants and activated complex (Glasstone, Laidler and Eyring 1941). However the problem of the determination of internal pressure in a liquid is not simple An equation to calculate the internal pressure of a liquid was deduced by Soonawala (1939) but the calculated value for compressibility of water differ markedly from the observed value The present paper attempts to give an equation which would make it possible to calculate internal pressure in a liquid.

The equation of state is obtained from the relation (Soonawala 1939 Max Planck)

$$p = -\frac{dF}{dv} = kT\frac{d}{dv}\left[\ln\int e^{-E\,pot/kT}\,dq_1\,dq_2\ldots\right] \quad \ldots(1)$$

The viscosity η of a liquid is given by (Glasstone Laidler and Eyring 1941)

$$\eta = \left(\frac{N}{V}\right)^{1/3} \frac{C\ RT}{\Delta E\ vap} (2\pi mkt)^{1/2}\ e^{\Delta E\ vap/nRT} \qquad (2)$$

where V = molar volume, m = mass of a molecule C = constant depending on the packing in a liquid, n = a factor which gives an indication of the size of the hole necessary for viscous flow Its value increases rapidly with temperature especially for associated liquids.

ΔE vap = The difference in energy per mole between the molecules in a liquid and in the gas and may be identified with E pot. potential energy for mole in equation (1)

$$\Delta E\ vap = E\ pot.$$

Other symbols are standard and need no explanation. From (2)

$$\eta = \frac{N^{1/3} CRT^{3/2}(2\pi\ k)^{1/2}(mN)^{1/2}}{V^{1/3}\ \Delta E\ vap} \times e^{\Delta E\ vap/nRT}$$

mN = Mol. wt. of the liquid = M

$$\frac{\eta}{N^{1/3}\ C\ RT^{3/2}\ (2\pi\ k)^{1/2}\ M^{1/2}} = \frac{1}{V^{1/3}\ \Delta E\ vap}\ e^{E\ vap/nRT}$$

For a given liquid at constant temperature $\frac{\eta}{N^{1/3}\ CRT^{3/2}(2\pi\ k)^{1/2}\ M^{1/2}}$ is a constant and may be denoted by A

$$\frac{\eta}{N^{1/3}\ C.R\ T^{3/2}\ (2\pi k)^{1/2}\ M^{1/2}} = A \qquad (3)$$

$$A\ V^{1/3}\ \Delta E\ vap = e^{\Delta E\ vap/nRT} \qquad (4)$$

Now ΔE vap is related to normal l tent heat per mole by th relation

$$\Delta E\ vap = \Delta H\ vap - RT \qquad (5)$$

where ΔH vap is norm l lat nt heat and RT is the correction for external work done in vaporising 1 mole of liquid. The vapour is assumed to behave as an ideal gas (Glasstone Laidler and Eyring 1941)

Now $\Delta H \text{ vap} = \Delta E \text{ vap} + RT$

$$1 = \frac{\Delta E \text{ vap}}{\Delta H \text{ vap}} + \frac{RT}{\Delta H \text{ vap}}$$

$\frac{RT}{\Delta H \text{ vap}}$ is a very small fraction (Saha & Shrivastava 1931) and may be neglected.

$$\Delta E \text{ vap} = \Delta H \text{ vap}$$

Now $\Delta H \text{ vap} = T(V \text{ vap} - V)\left(\frac{dP}{dT}\right)_{Sat.}$ (Saha & Shrivastava 1931

where V vap = Molar volume of the liquid in the vapour state and $\left(\frac{dP}{dT}\right)_{Sat.}$ = variation of saturated vapour pressure with absolute temperature

$$\Delta E \text{ vap} = T\,(V \text{ vap} - V)\left(\frac{dP}{dT}\right)_{Sat.} \qquad (6)$$

At a constant temperature V(vap) molar volume of the liquid in the vapour state will be related to molar volume of the liquid by the relation

V vap = a, V where 'a is a constant depending on temperature and is constant if temperature is constant

$$\Delta F \text{ vap} = T\,(a-1)V\left(\frac{dP}{dT}\right)_{Sat}$$

Substituting this value of ΔE vap in equation (4) we have

$$A\;T\;(a-1)\;\left(\frac{dP}{dT}\right)_{Sat.}\;V^{5/3} = e^{\Delta E \text{ vap}/nRT}$$

or

$$e^{-\Delta E \text{ vap}/nRT} = \frac{1}{A.\;T\;(a-1)\left(\frac{dP}{dT}\right)_{Sat.}V^{5/3}}$$

$$e^{-\Delta E \text{ vap}/kT} = \frac{1}{A^{nN}\;T^{nN}\;(a-1)^{nN}\;\left(\frac{dP}{dT}\right)_{Sat.}^{nN}\;V^{5nN/3}}$$

$$e^{-E \text{ pot}/kT} = e^{-\Delta E \text{ vap}/kT}$$

$$= \frac{1}{A^{nN}\;T^{nN}\;(a-1)^{nN}\;\left(\frac{dP}{dT}\right)_{Sat.}^{nN}\;V^{5nN/3}}$$

Substituting the value of $e^{-E\ pot/kT}$ in equation (1) we have

$$p = kT\frac{d}{dV}\left[\ln\int\frac{dV}{A^{nN}\ T^{nN}\ (e-1)^{nN}\left(\frac{dP}{dT}\right)_{Sat.}^{nN}\ V^{5nN/3}}\right]$$

$$\text{Let}\ \frac{1}{A^{nN}\ T^{nN}\ (e-1)^{nN}\left(\frac{dP}{dT}\right)_{Sat.}^{nN}} = X$$

X is a constant if temperature is constant and is independent of V

$$p = T\ \frac{d}{dV}\left[\ln\frac{1}{X} + \ln\int V^{-5nN/3}dV\ \right]$$

$$= kT\ \frac{d}{dV}\left[\ln\frac{1}{x} + \ln\left(\frac{3}{5nN-3}V^{-5nN/3+1}\right)\right]$$

$$= kT\ \frac{d}{dV}\left[\ln\frac{1}{x} + \ln\frac{3}{5nN-3} + \left(\frac{-5nN}{3}+1\right)\ln V\right]$$

$$= kT\ \frac{d}{dV}\left[\frac{-(5nN-3)}{3}\ln V\right]$$

$$= \frac{-(5nN-3)}{3}\ kT\ \frac{d}{dV}(\ln\ V) = \frac{-(5nN-3)\ kT}{3V}$$

N is Avogadro's Number 5nN is therefore very large and 3 may be neglected in comparison with 5nN

$$p = -\frac{5nNkT}{3V} = \frac{-5n\ RT}{3V} \qquad \ldots\ldots (8)$$

$$\text{Let}\quad \frac{3V}{5n} = x \qquad \ldots\ldots (9)$$

$$\text{Then}\quad p = -\frac{RT}{x} \qquad \ldots\ldots (10)$$

The negative sign indicates that the internal pressure is negative and is therefore due to the force of cohesion between the molecules in the liquid.

Equation (9) resembles the ordinary gas equation except the negat

The value of n for water which is an associated liquid increases rapidly with temperature. Thus at 0 C n=2.01 and at 50 C=2 81. The value of n at 20 C may be taken as the average of the values of n at 0 C and 50 C. Thus at 20°C n=2.41. Expressing R in atmosphere cc/degree, the internal pressure at 20°C and 1 atm. external pressure comes out to be

$$p = -\frac{5\times 2.41\times 22400\times 293\times 0\ 9982}{3\times 18\times 273} = -5\ 374\times 10^{4}$$

atmospheres.

Now $\Delta V = \frac{dV}{dp}\Delta p$

From equation (9) $\frac{dp}{dV} = \frac{RT}{x^2}$

$$\Delta V = \frac{x^2}{RT}\ \Delta p.$$

$$\text{C compressibility} = \left(\frac{\Delta V}{\Delta p}\right)\Big/ V = \frac{\Delta V}{V\,\Delta p}$$

$$= \frac{1}{V}\frac{x^2}{RT}$$

$$= \frac{1}{V.RT}\left(\frac{3V}{5n}\right)^2$$

$$= \frac{9V}{25\ n\ \ RT} \qquad \text{..} \qquad (11)$$

Compressibility (at 20 C and 1 atmosphere per sq cm.) for water

$$= \frac{9\times 18\times 273}{25\times 2.41\quad 2.41\times 22400\times 293\times 9982}$$

$$= 46.3\times 10^{-}$$

The experimental value of compressibility for water 20 C and 1 atmosphere per sq cm (which is approximately 1 kgm. per sq cm) is 45.3×10 (Childs). The agreement between the calculated and experimental value is satisfactory

CALCULATION OF n FOR A LIQUID

The conventional method employed to determine n is to compute viscosities from equ tion (*) by use of integral and half integral values of n from 2 to 5 and to plot the resulting figures for log η against 1/T. For any value of n the plot is either a straight line or in some cases, a curve slightly convex toward 1/T axis. The value of n that gives a plot parallel to the straight line of the computed data for log η against 1/T is taken as the correct one

The equation (11) provides a simple method to calculate the value of n for liquid if the compressibility data for the liquid is known.

For Benzene t 20 C and 1 atmosphere per sq cm. pressure the compressibility $C = 91 \times 10^{-6}$

From equation (11) $n^2 = \frac{9V}{25RT\ C}$

Mol. wt. for Benzene = 78 Density of Benzene at 20° C = 0 88 gr per cc.

$$n^2 = \frac{9 \times 78 \times 273}{25 \times 22400 \times 293 \times 0\ 88 \times 91 \times 10^{-6}}$$

$$n = \left[\frac{9 \times 78 \times 273}{25 \times 22400 \times 293 \times 0\ 88 \times 91 \times 10^{-6}}\right]^{1/2} = 3\ 821$$

From an examination of the results of number of substances it is found that for most non-associated liquids 'n lies between 3 and 4 (Glasstone Laidler and Eyring 1941 p 494) The value of n obtained from equation (11) is thus in fair agreement with the value of n = 3·3 for benzene

For carbon tetrachloride the compressibility at 20 C and 1 atmosphere per sq cm. = 90×10^{-6}

Molar volume for carbon tetrachloride at 19 9 C = 97

$$n = \left[\frac{9\ \ 97\ \ 273}{25 \times 22400 \times 293 \times 90 \times 10^{-6}}\right]^{1/2} = 4.1$$

The value of n = 4.11 for carbon tetrachloride is in agreement *with the value of n = 3 to 4 for most of th* non-associated liquids It will be seen that equation (10) can be used to calculate the internal pressure in a liquid whil equation (11) can be used to calculate the compressibility of a liquid and determination of r a factor which determines th size of a hol necessary for viscous flow

ACKNOWLEDGEMENT

The author wishes to express his grateful thanks to Prof M.F Soonawala of Maharaja s College, Jaipur for advice encouragement.

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21
SERIES TRANSDUCTORS

By

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[Abstract The theory of transductors based on [illegible] edge of electromagnetism is discussed critically [illegible] analyses are reviewed with a view to express [illegible] which are commonly tackled in research]

INTRODUCTION

The Transductor is an electromagnetic device in which the inductance of an A C winding can be controlled by varying the magnitude of direct current flowing in a coil [illegible] with the A. C winding This previously known as [illegible] Reactors" have been in use for many years[1] [illegible] confined to power engineering. Owing to the [illegible] of magnetic materials with desirable characteristics [illegible] m tal rectifiers (especially selenium rectifiers) [illegible] characteristics and reliability the transductors have become widely popular in both Electronics and power engineering. The applicability of Transductors in electrical engineering [illegible] a unique place th t one[2] has even suggested the new name Magnetonics for this branch of study Transductors in power engineering are used mainly for automatic [illegible] measuring heavy direct currents or high [illegible] In lectronics, Transductors are used as magnetic amplifiers [illegible] precision instrument work servo-mechanism and [illegible] types of control and metering The most attractive features of Transductors are its useful form of control characteristics the ruggedness of construction and reliability in operation.

During the second world war (1939-45) German Scientists used magnetic amplifiers quit successfully in various equipments[3] It may be said that most [illegible]

development of Transductors started since the end of the last world war In certain aspects magnetic amplifiers became comparable with the thermionic amplifiers since these are able to mix and amplify D C powers of as low as 10^{-8} watt. Using mumetal cores and self-excitation or positive feedback the power amplification can be increased to 5000 or more Inspite of the fact that magnetic amplifiers can be used successfully for precision instrument work and second-harmonic modulators or other automatic controls, the pplication of this is seriously limited by the large time taken for the output to respond to the change of input d c signal.

This paper however is intended to describe the basic principles and a review of the present theory of series Transductors Various authors have analysed Transductors in great many aspects of their behaviour The principal aspects are

(*a*) A simple series Transductor with comparatively low impedance in the control circuit.

(*b*) A simple series Transductor with comparatively high impedance in the control circuit.

(*c*) A series Transductor with separate feedback windings

(*d*) A series Transductor with self-saturation.

(*e*) Transductors with second harmonic feedback.

and (*f*) A parallel Transductor with conditions of operation as mentioned in (*a*) (*c*) and (*d*).

From the above it is seen that such ramifications of Transductors can hardly be summerised in one paper and therefore we shall mainly confine our discussions to series-transductor circuits. The list of symbols to be used is given below

LIST OF PRINCIPAL SYMBOLS

V — Voltage across the Transductor elements

I_d — D C component of current in the control circuit

i_d — D C component of current in the control-circuit with self-excitation

I_{av} — Average current in a c circuit after rectification.

i_a — Instantaneous value of current in the a. c. circuit

I_o — Peak magnetizing current when K=1 and $\lambda=0$

I — Current corresponding to ϕ the displacement of the flux axis.

P — "Mean power amplification.

n — $\frac{\sqrt{R^2+X^2}}{R}$

N — No. of turns in a. c. winding on each Transductor element.

N_d — No. of turns in d. c. winding on each element.

N_f — Self-excitation turns on each element.

R — Total resistance in the a. c. circuit.

X — Total reactance in the a. c circuit

R_d — Total resistance in the control circuit.

L_d — Inductance of the control circuit.

ϕ_a — Average value of flux between 0 and 2π for a single core or displacement of the flux axis.

ω — Angular frequency of supply

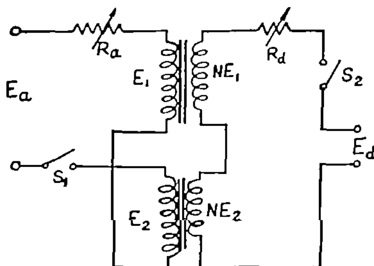


FIG 1

BASIC PRINCIPLES

Fig. 1 shows the basic Transductor circuit using two cores. E is the a. c voltage applied across the two windings in series, and E_d the direct voltage is applied across the two secondary windings in opposition in order that the transformer action on the d c windings is eliminated. The a c windings are commonly termed as load windings or output windings and d c windings as control windings. There is a load resistance R_a in the a c circuit and R_d is the resistance in the d c circuit such that R_a R_d. The two transductors are assumed to be identical in all respects In the following discussion B–H characteristic of cores is assumed as shown in Fig 1 (a) Now with S_1 closed and S_2 open, the

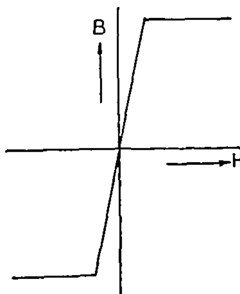


Fig 1a

current in the a. c circuit with normal supply voltage E_a, is negligibly small. This current produces a very small voltage drop across R_a consequently $E_1+E_2=E_a$ To write the circuit equation in general form

$$E_a=E_1+E_2+I\ R_a \quad \ldots\ldots \quad (1)$$

If direct current of magnitude I_d now flows when S_2 is closed, the fluxes produced in the two cores due to I_d will be in opposite directions since the d. c windings are connected in opposition. Thus at any instant the d c. flux will help the a. c flux in one core and oppose the a. c flux in another And at a particular instant the core 1 (say) saturates and E will become zero This may be termed as the conducting period, whence $E = E_1 + I_a R_a$ This shows that full voltage E_1 is switched on across the load and I_a at this instant is much greater than I in equation (1).

Again the general ircuit equation for d. c circuit,

$$NE_1 = NE_2 + E_d - I_d R_d \qquad (*)$$

where $N = {}^{N}/N_a$

The above equation is valid for non-conducting period i. e. when neith r core is saturated But when core 1 is saturated, $NE_1 = 0$ thus

$$0 = NE_2 + E_d - I_d R_d \quad \text{or} \quad I_d R_d = NE_2 + E_d \ldots \quad (3)$$

The above consideration shows that for $E = 0$ an increment in I_a occurs and since $NE = 0$ equal increment in I_d must occur in the control circuit in order that equation (3) is satisfied Of course the magnetising current is ignored Hence it may be written as,

$$I_a N = I_d N_d \quad \text{or} \quad I = NI_d \ldots \quad (4)$$

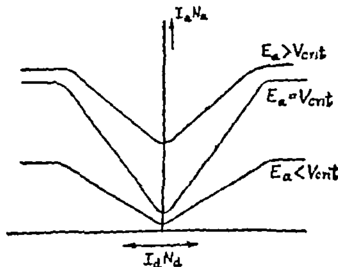


FIG 2

This is the most important control characteristic of a Transductor and signifies the magnetic amplifier operation If a curve is drawn (I N . $I_d N_d$) it can be shown that the equation (4) is only true for the linear part. The linearity is sensitive to supply voltage changes as is indicated by the different curves. (fig. 2.) Another interesting feature is that the characteristics are insensitive to the polarity of direct voltage E_d

CRITICAL REVIEW OF TRANSDUCTOR THEORY

Here we shall consider a series Transductor with comparatively low impedance in the control circuit and with or without feedback In the analysis of the theory of Transductors, certain assumptions are necessary in order to bring out the design features in a simpler form so that the theory could be conveniently used in practice. Although it should be borne in mind while making assumptions that no appreciable error is introduced in the theoretical and experimental results obtained therefrom

A rigorous analysis of Transductors is extremely difficult because of nonlinear and multivalued character of the magnetization curve Therefore the assumptions generally made by different authors are

(*i*) The magnetisation characteristic of a core consists of a very high permeability in the unsaturated region followed by abrupt transition to complete saturation (Fig. 1a).

(*ii*) Magnetising current is ignored

(*iii*) The unsaturated reacta nces of Transductors are so large compared with R_L that the phase difference between the applied voltage and that across the transductor is neglected.

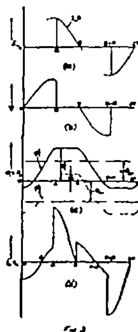
(*iv*) (*a*) Control circuit impedance is assumed to be neg ligibly small compared to R_L This assumption complies with certain requirements in industry and automatic controls.

(*b*) Control circuit impedance is comparatively high and this assumption finds its application in measuring heavy direct current or high voltage D C. [R ference (10)].

In addition to the above almost all the authors on this subject assume leakage reactance hysteresis and eddy current losses negligible Also the forward resistance of rectifiers is assumed to be small while reverse resistance is ve y high.

In a paper[4] by A. G Milnes assumptions made fall in categories (*i*) (*ii*) ( ), (*iv*)a and from the basic assumptions, flux wave forms were derived and equations were developed for magnetomotive forces operating at every instant in the cycle

Fig. 3 (a) shows the general wave shape of supply voltage E_s At an instant α of the voltage cycle the core saturates and so voltage across the transductor drops to zero [Fig 3 (b)] and the total voltage ($E - I_s R$) appears across the load resistance R_L (Fig 3 (a) shown full line) Instantaneous values of flux in the two cores between 0 and α (i e when the cores are unsaturated) are say ϕ_1 and ϕ [Fig. 3 (c)]. Between α and π the core remains saturated and the value of flux in core 1 is ϕ and core 2 is ϕ_0 [Fig. 3 (c)] During the interval π and $\pi+\alpha$, the cores are again unsaturated Again in the time interval $\alpha+\pi$ and 2π the core 2 is saturated but core 1 is unsaturated.



Let the supply voltage be $E_s = E_m \sin \omega t$. The a. c. windings are connected in series and the control windings are in series opposition (Fig 1) therefore

$$N \left(\frac{d\phi}{dt} + \frac{d\phi_2}{dt}\right) = E_m \sin\omega t. \times 10^8 \quad \ldots(5)$$

and

$$N_c \left(\frac{d\phi_1}{dt} - \frac{d\phi_2}{dt}\right) = 0 \quad \ldots(6)$$

Referring to the above assumption, the equation (6) shows that when the flux in one core remains constant due to saturation, the flux in the other core shall also remain constant The maximum peak voltage E_s that can be applied to the transductor without causing saturation & I_c being zero is

$$E_s = \frac{2\phi_s \omega N}{10^8} \quad \text{where } \phi \text{ is the saturation flux per core}$$

If $K = \frac{E_m}{E_s} = \frac{\phi_m}{\phi}$ it can be shown that solution of equations (5 & (6) within limits of $\omega t = 0$ & $\omega t = a$ are

$$\phi_1 = \phi_s + K\phi_s \cos \; - K\phi_s \cos \omega t \quad \ldots (7)$$

$$\phi_2 = - K\phi \;\; \cos \;\; \omega t - (1 - K)\phi_s \quad (8)$$

The average flux in core 1 sav is equal to $\frac{1}{2}(\phi_s - \phi_a)$ (fig. 3c) where, $\phi_a = -K\phi_s \cos a - (1 - K)\phi_s$

Putting $\omega t = a$ in equation (8), we have

$$\phi \;\; = \tfrac{1}{2}\phi \;\; [(2-K)+K \;\cos a] \quad \ldots (9)$$

This quantity is of interest since variation of ϕ_{av} determines the time constant of transductor

CIRCUIT SENSITIVITY

The circuit sensitivity was defined as the $\frac{d\, I_{av}}{d\, I_c}$ Where I is the average rectified load current and was found to be equal to

$$\frac{d\, I}{d\, I_c} = \frac{X/R - 1}{X/R + \frac{1}{2}\pi} \quad \ldots (10)$$

with $\lambda = 0$ where $\lambda = \frac{N_f}{N}$ = self-excitation factor

This shows that the current amplification is independent of K or the value of A. C. supply voltage The above also shows that the current amplification of a simple transductor is not constant and equal to $\frac{N_a}{N}$ as elementary treatment suggests but that the amplification depends on the ratio of X/R of the A C circuit

POSITIVE FEEDBACK

The sensitivity of a simple transductor m y be increased by using the rectified output current I_s to produce an m m f which aids control m m f. This is known as "positive feedback or "self-excitation In (Fig. 4 th transductor contains additional

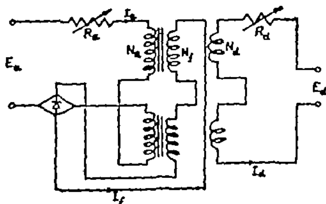


FIG 4

windings N which are placed on the core such that it is magnetically parallel with th control windings and hence immune from transformer interaction. The self-excitation winding provides the feedback and is connected in series with a rectifier in the load circuit of the transductor The load current I_s thus passes as rectified current I through the winding N_f producing feedback in the Transductor

The degree of feedback in a transductor is increased or decreased by corresponding alteration of the no of turns N The function of feedback amp-turns is to decrease or increase the D C. excit tion and thus ffect the resultant transductor chara teristics Hence the feedback is called "undercompensated if the feedback amp-turns is less th n the D C. amp-turns for I_d being positive. And the transductor feedback is called overcompensat

if the feedback amp-turns exceeds the D C amp-turns for I_d being positive This overcompensation characteristic produces an instability loop in the resultant control characteristic such that I_a jumps from a low value to a higher value as I_d goes positive and jumps in the reverse direction as I_d goes negative

Therefore, the boundary between undercompensating feed back and over-compensating feedback is determined by the $N_f/N = \lambda$ = self excitation factor In the case of an ideal transductor critical value of $\lambda = 1$ for a series transductor and 0.5 for a parallel transductor

The Fig. 5 shows the characteristic of an undercompensated feedback transductor The positive branch shows increased control

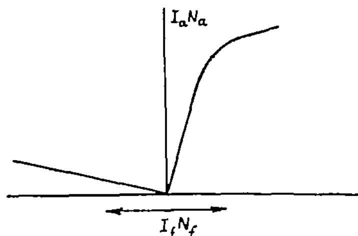


Fig 5

sensitivity while the negative branch shows reduced sensitivity This also indicates that the range of linear control is shortened in the positive branch but lengthened in the negative branch With this form of feedback high power gain is possible The current sensitivity is of the form

$$\left(\frac{d\,I_w N}{d\,I_d N_d}\right) = \left(\frac{1}{1-x\lambda}\right)x \qquad \ldots\ldots\ldots (11)$$

where $\chi = \dfrac{N/R - 1}{N/R + \frac{1}{2}r}$ If the reciprocal of the current amplification is considered for complete self-excitation $N_f = N$ then we have

$$\frac{d\,I_d}{d\,I_w} = \left(\frac{\frac{1}{2}r+1}{X}\right)\left(\frac{N}{N_d}\right)R.$$

Thus for a given change of control current $\triangle I_d$ the corresponding change of transductor output voltage is

$$\triangle V = R\left[\left(\frac{d\,I_{av}}{d\,I_d}\right)(\triangle I_d)\right]$$

$$\text{or} \quad \frac{\triangle V}{\triangle I_d} = \left(\frac{X}{\sqrt{r+1}}\right) \quad \frac{N_d}{N} \quad \ldots \quad \ldots \quad \ldots \quad (12)$$

Thus the equation (12) is seen to be a constant (independent of R) for any particular transductor Therefore a full self-excited transductor gives, for a certain change of control urrent, a defi it change of output, voltage whatever the load resistance may be This is contrary to the behaviour of a transductor without feedback (Eq 10) which gives, for a fixed control current, output current varies only slightly with the load resistance

TIME CONSTANT

Since the transductor circuit is associated with varying fl x density with respect to time the time of response of the chang in load current with change in control current is a determinabl factor The time constant of transd ctor depends on the change of the averag core flux ϕ_{av} with change of I_d Since th ϕ_{av} is positive in one core and negative in the other and since th tw d c. windings re connected in series opposition the m. f induced by the change of average core flux in the two d. windings are additive. But there is no resultant e.m.f cross the a.c. wi di gs.

For a resultant load there can be no time lag between control current, th related ϕ_{av} and the corresponding output urrent It follows therefore, that th exponential time lag between the d voltage and d c c rrent constitutes the sol time lag of the transductor circuit With ref rence to th condition just stated, the quation for the rise of current I_d in th control circuit

$$E_d = I_d R_d + 2N_d\left(\frac{d\phi_{av}}{d\,t}\right) 10^{-8} = I_d R_d + 2N_d\left(\frac{d\phi_{av}}{d\,I_d}\right) 10^{-8}$$

from this th tim constant can be derived as follows:—

$$T = \frac{2N}{R_d}\left(\frac{d\phi_{av}}{d\,I_d}\right)10^{-8} \quad \ldots \quad \ldots \quad \ldots \quad (13)$$

The power amplification is defined as $P = \left(\frac{d\,I_L}{d\,I_d}\right)^2 \frac{R}{R_d}$

And if X/R is very large $\frac{d\,I}{d\,I_d} \frac{N}{N_d}$ tends to a limiting value $\left(\frac{1}{1-\lambda}\right)$ and it can be shown that

$$P = 4f\,T\left(\frac{1}{1-\lambda}\right) \quad \ldots \quad \ldots \quad \ldots \quad (14)$$

For complete self-excitation the Eq (13) becomes,

$$T = \left(\frac{L_d}{R_d}\right)\left[\frac{/_1}{\pi + \theta -}\right]$$

here θ corresponds to an angle at which $I_a = 0$

when, $= \pi$ $\theta = \pi/_2$, $T = \frac{L_d}{R_d}$

also $= 0$ $\theta = 0$ $T = \frac{1}{2}\,\frac{L_d}{R_d}$

Thus for the limiting condition of full self-excitation the time constant of a transductor at low output current is equal to L_d/R_d For all the conditions ($\lambda < 1$) the time constant is less than this value This also reduces current amplification This reduction of the time constant when $\lambda < 1$ is at the expense of a reduction in the ratio of P/T (Eq 14); therefore a high degree of self-excitation is preferable in most applications.

It is also found that the ratio of time constant to the current amplification is independent of K, where X/R is very large the ratio becomes proportional to R Some time constant measurements for a transductor with $\lambda = 0$ it is seen that for low output currents I the time constant is high and that at high output currents the current amplification and the time constant both decrease considerably These are imperfections caused by the core characteristics and are not predicted by the theory

The assumptions made by Milnes reduces the utility of the analysis to some extent in it s application to practical problems as pointed out by Hudson Since most core materials show considerable curvature at the knee of the B/H curve the transient changes that occur at the cut-off cannot be ignored. Thus the assumptions made by Hudson are different from those of Milnes in that, the phase shift between E_a and V is not neglected and also that the magnetising current is not ignored.

When the flux reaches the knee of the magnetisation curve (Fig 6 the whole of the supply voltage appears across the load resistance R_a since cores 1 and 2 are both saturated in the alternate half cycles. The transductor regains control when the load current falls to $(I_o - I_x)$ At this point the transient changes occur due to the flux changes the eq

$$E_m \sin(\omega t - \beta) = i\ R + X/\omega\ \frac{d\,i_a}{d\,t} \qquad (16)$$

where $\beta = \sin^{-1}\ \frac{R}{\sqrt{R^2 + X^2}}$ denotes the phase difference between supply and transductor voltages.

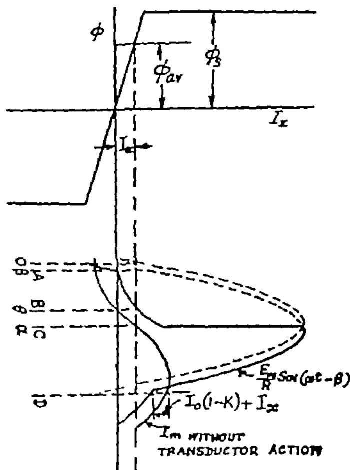


FIG 6

The solution of equation (15) gives the value of I_a with proper substitution of values of constant C and magnetising current

$$I_a = -KI \cos \omega t \mp [I_a(1-K) - I] e^{-(R/x)\omega t} \quad (16)$$

The effect of the exponential term is to displace the I_a during the operating period of the transductor and to shift the point ϕ at which the current is zero. The maximum possible value of $\omega t = \pi$ and since R/X is small $e^{-(R/x)\omega t} \simeq 1$ and hence

$$I = -KI \cos \omega t \mp [I_a(1-K) - I] \quad .. \quad (17)$$

The equation for output current I is obtained as,

$$I_{av} = 2K \frac{I_a}{\pi}\left[n(1-a) \frac{a}{2n} + f(a)\right] \ldots\ldots \quad .. \quad (18)$$

Since the control winding links both cores and has a low impedance to harmonic currents there will be a circulating current when saturation occurs in one core which will prevent the flux change in the second core. As Milnes points out (Eq 0) the control current will be the mean value of the magnetising m. m. f for any one core.

Hence

$$I_d = \left[\frac{N}{N_d}\right] I + \frac{2}{\pi} KI \left[\frac{\lambda}{N_d}\right]\left[n(1-a) - \frac{a}{n} + F(\ )\right] (19)$$

It will however be noticed that the Eq 18 is independent of λ and also that

$$I_d = I_d + \lambda I \left[\frac{\lambda}{N_d}\right]$$

where I_d is now the control current with self-excitation. The equation for I_d for $a \geq 1$

$$I_d = \frac{N}{N}\left[I - \frac{2}{\pi} KI \left\{\frac{(1-\lambda)}{2n} + \lambda\right\}\right] \ldots \quad (20)$$

an interesting case occurs when $\lambda = 1$

$$I_d = \left[\frac{\lambda}{N_d}\right]\left[I + \frac{2}{\pi} KI \left\{F(a) - f(\ )\right\}\right] \ldots\ldots \quad (21)$$

An interesting feature is that I_{av}, I_d and I_d are all expressed in terms of the magnetising current for zero load namely $\frac{2}{\pi} KI_m$

when $a = 1$ I_{av} becomes the magnetising current $\frac{2}{\pi} KI_a \left(1 - \frac{1}{2n}\right)$

It is less then $\frac{2}{\pi} KI$ owing to the load resistance which introduce the $\frac{1}{2n}$ term.

A B/H Curve is shown in (Fig. 7) A pair of straight lines B and C can be fitted to this, but there are small discrepancies at low value of flux density and quite large depart res near the knee of the curve a has been defined as $\frac{I_s - I}{KI}$ and it m y also be written as, $a = \frac{\phi_s - \phi_{av}}{K\phi_s}$ which now determines the flux levels and

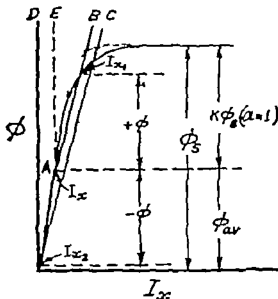


FIG 7

this eq ation will then be tru for a B/H urve which is not linear upto the saturation point. Since the B/H curve d termines I and I this must have some effect on I_{av}, I_d and i_d (equations 18 19 and 20) But unless I changes appreciably with a I_{av} I not substantially affected It therefore follows from equations 19 and 20 that I_d and i_d are dependent on the shape of B/H curve and a closer approximation to the true characteristics is obtained by inserting the values of I derived from xperimental B/H curve ϕ_{av} corresponding to the required value of a, in th equations 19 & 20

Th flux levels in the two cores of the Transductor at any instant will be $\phi_{av} \pm \phi$ where ϕ is th flux change Since the slopes at these flux levels are different, a circulating current flows in the

control circuit such that the mean value of I is given by $\frac{1}{2}(I_{x1}-I_{x2})+I$ where I_{x1} and I_{x2} correspond to two fluxes and I correspond to ϕ_{av}. The effective B/H curve is therefore of the from shown in Fig 7. The construction of this curve is given elsewhere.

In most of the theories developed by other authors (*Reference* 1 7 8) a rectangular magnetisation curve was assumed and the basis of their an lyses falls mainly in the categories (i), (ii) (iii) (iv). *Although the form of presentation in these papers is comparitively* simple and provides scope for clearer understanding of the magnetic amplifier phenomen. The results obtained are simpler than those described before but since they suffer from being to simple these are not presented h re. Besides the conclusions derived from their experiments are to a certain extent agreeable with the present knowledge of Transductor theory.

ARRANGEMENT OF THE WINDINGS

A Transductor with two separate magnetic cores is seldom used in practice. The more common arrangement of cores and windings are as shown in Fig 8. The factors governing the design of arrangement of cores and winding are leakage reacta ce s ving in winding space etc.

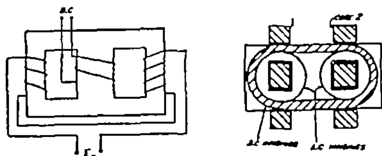


Fig 8

The magnetic properties of the core materials should be such that hysteresis and eddy-current losses are minimum, the saturation flux density must be high and the ideal B/H curve should be obtainable. These characteristics must be adhered to for special high gain amplifiers.

It has also been found that the construction of core laminations affect the performance of a transductor a great deal owing to the following facts :—

The normal method of staggering the T's and U's or E s and I s produces air gaps at the joints thus there is concentration flux in one lamination [Fig. 9(a)], causing local saturation of iron and reduces the sharpness of bend in the B/H characteristic

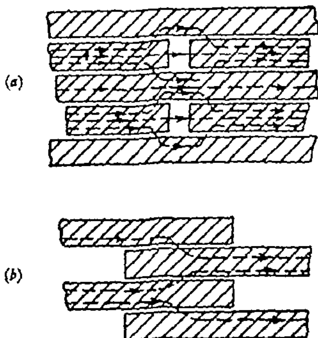


FIG 9

Therefore if the butt joint is overcome by not producing any air-gap, a uniformity in the flux path may be obtained [Fig. 9(b)]. It was found to have secured considerable improvement on the characteristics of a magnetic amplifier

CONCLUSION AND REMARKS

1 The linearity of the control characteristics of a transductor is dependent upon the supply voltage th self excitation factor λ, the B/H characteristic of the core material the pattern of the core and the load.

The characteristic is primarily independent of frequency of a. c power supply Secondary frequency effects such as hysteresis loss & eddy current effects in the core or leakage flux of the windings m y effect the characteristic.

2 The well known amp-turns relation ($I_c N_c = I_d N_d$) differs slightly (see eq 10) from the fundamental current transformer relationship The magnitude of deviation depends on the transductor construction the form of the actual B/H curve for the core material and the ratio X/R for a transductor

3 The time constant or the response time of a transductor to the input d c signal voltage is dependent on λ the self-excitation factor the frequency of the a. c power supply the impedance of the control circuit and also the overall power gain of a transductor in the operating zone

The ratio of power gain to time constant is independent of K but proportional to the load resistance when X/R is large

It is also seen that transductors without any feedback have high time constant for low output currents. While at high output currents both current amplification and the time constant of a transductor decrease considerably

From the above conclusion, it is evident that the desirable characteristic depend much on the type of core material chosen and also on the caref l design and construction. Reviewing the literature of this field one immediately notices a common property of these papers In most cases the author accepts a mathematical defeat and makes rash assumptions regarding forward and reverse resistances of the rectifier and the B/H relationship of the magnetic material The performance equations derived on the basis of these ass mptions establish a clear and simple physical picture but cannot be used to predict the exact performance of the transductor amplifier Non-linearities of transductor amplifier are just beginn ing to be studied[11] to be able to predict exactly what output will be obtained for a given control current

In this connection it may be noted that to obtain high power gain hysteresis and eddy current losses cannot be ignored in the design of magnetic amplifier This involves exact determination of Dynamic *hysteresis loop for a core material Recently the*

analysis of a transductor amplifier is focussed on the accurate determination of the dynamic hysteresis loop and its effect on the performance of Transductor amplifiers[11]

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22

ISOMERISATION OF BENZYLAMINE THIOCYANATE & METHYLAMINE THIOCYANATE

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In efforts to correlate th lkalinity of the bases with the extent of isomerisation of thiocyanates in the pres nce of solvent and without it the present work is originated.

Benzylamine thiocyanate m p. 100 – 101°C a thiocyanate of the base having the dissociation constant 2.4×10^{-4} at 25 C is prepared Study of its isomerisation to substituted thiocarbamid is undertaken.

Methylamine thiocyanate m.p 67°C a thiocyanate of a base having the dissociation constant 5.0×10^{-4} at 25°C is prepared. The isomerisation of this thiocyanate is also undertaken. Th isom risation in solution as well as in the absence of the medi m was followed by estimating thiocyanate left behind unchanged fte a certain interval of time

(a) In aqueous alcoholic solution (1 1) at 85°C th isom risation in both cases could not be detected even qualitatively a point in conformity with th established rule "Stronger the base slowe is the isomerisation of its thiocyanate in aqueous alcoholic solution at 25 C Dilute sulphuric acid in case of methylamine thiocyanate only was detected to accelerate the isomerisation in queous alcoholic solution and th isomerisation was detected only qualitatively But in case of Benzylamin thiocyanate sulphuric acid was found to be immaterial

(b) A normal solution of benzylamine thiocyanat in ethyl ne-glycol solution at 140°C isomerised slowly After heating for bout 40 hours the reaction seemed to stop Heating for another 8 hours

The above method for estimating thiocyanic acid was followed in case of both the amines

St dy f Isomerisation of Benzylamine th ocyanate in solid st te i e. without me ium at 100°C and 120°C —Several test tubes having definite amounts of solid benzylamine thiocyanate arranged in a rack w re put in a bath maintained at a particular temperature After definite intervals of time known weights of the heated residue were estimated for thiocyanic acid contents as described above

Study f Isomerisat on of Benzylamine th ocyanate n ethylene glycol an 100°C —Normal solution of benzylamine thiocynate was prepared in ethylene glycol and 5 c c of the solution is titrated against standard silver nitrate solution in presence of 10% nitric acid using iron-alum as the indicator The solution was refluxed in a conical flask fitted with an air condenser and kept in an oil bath maintained at 140 C After definite interval of time 5 c c of the solution is taken desulphurised by alkaline cadmium sulphate as before filtered washed till free from thiocyanate contents and then determined by Volhard's method

Study of somerisat on f Methylamine th ocyanat in sol d state e without any med um at 120°C —This was lso studied in the same manner as in the case of Benzylamine thiocyanate

Effect of sulphuric acid on the isomerisation of methylam ce th cyanate and benzylam ne thiocyanate at 85°C —103 c c of N Methylamine thiocyanate solution in 50% alcohol was prepared and 40 c.c of O 1 N sulphuric acid is added to it and the mixture i refluxed on a water b th with a condenser The isomerisation was studied in the same manner as before

It was found after refluxing for 18 to 20 hours that in presence of sulphuric acid too the isomerisation was very slow and the change is so littl that it cannot be determined quantitatively but only qualitatively tested

In case of benzylamine thiocyanate no isomerisation was detected even qualitatively after 20 hours heating.

TABLE I

Results of the isomerisation of N N/2 and N/5 Benzylamine thiocyanate at 85 C.

S N	Time	% of benzylamine thiocyanate contents	Velocity Constant
1	2 hours	No isomerisation	No isomerisation
2.	4		"
3.	6	"	
4.	8 "	"	"
5.	10 "		"
6.	12 "	"	"
7	14 "		"
8	16 "		"
9	18 "	"	"
10	20 "		"

Conclusion —From the above table it is clear that even after 20 hours heating, no isomerisation has taken place in case of all the concentrations mentioned above The isomerisation to substituted thiourea was not even qualitatively detected

Results of the isomerisation of N N/2 N/3 methylamine thiocyanate t 85 C

Results obtained in this case are similar to the results obtained in case of Benzylamin thiocyanate at all the concentrations and hence the conclusion arrived at in case of Table No I also holds true here.

TABLE II

Results of th isom risation of Benzylamine thiocyanate in melt at 100° C.

S. No.	Time	% of benzylamine-thiocyanate contents	Velocity Constant
1	½ hour	93 98	0 002073
2.	1 "	92.96	0.001317
3.	1½ "	90 66	0.00100
4.	2 "	88.24	0 001042
5	½ "	84.63	0.001111

Conclusi n —From the table it is clear that isomerisation in this case is very slow even in melt.

TABLE VII

Results of the isomerisation of N/15 Methylthiocarbamide to Methylamine thiocyanate at 85 C

S. N	Time	% f methylami e-thiocyanate formed	V locity Constant
1	10 hours	7 59	0 0001316
2.	20 ,,	8 347	0 00007273
3	30 ,,	9 813	0 00005744
4.	40	12.06	0 00005364
5	50 ,,	13 50	0 00004867
6	60	15.1	0,00004548
7	70	16 01	0 00004327
8.	80 ,,	18 11	0 0000416

Conclusion—From this table it is clear that methylthiocarbamide is isomerising to methylamine thiocyanate slowly

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MAGNETIC STUDIES ON TARTRATES

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[Abstract. Mean susceptibility for several powdered Tartrates has been measured. The result has been discussed in relation to the deformation produced on the tartrate ion by its environments and hence its influence on their diamagnetism]

INTRODUCTION

It is well-known that crystalline electric fields can produce deformations in ions and radicals in crystal lattices The influence of these deformations on diamagnetism of ions or radicals is quite feeble and hence much attention has not yet been focussed on the study of this effect.

A survey of the experimental results of inorganic carbonates and nitrates reveal that diamagnetism of $(NO_3)^-$ or (CO_3) radicals is influenced to a measurable degree by the character of the environment of ions surrounding the radical The following table (I) made with the help of Angus (1932) value of metallic ions and the experimental values of Nilkantan (1928) for the compounds makes it clear that spherically symmetrically ions lik Na K Ca^{++} Sr^{++} and Ba^{++} which surround the radicals $(NO_3)^-$ or (CO_3) can produce a change in the diamagnetism f $(NO_3)^-$ and $(CO_3)^-$ radicals

TABLE I

Mean susceptibility $(-\overline{X} \times 10^{-6})$ of (NO_3) radical from powder crystals of			
$NaNo_3$	KNO	AgNO	$Sr(NO_3)$
21.9	*0 9	*0.3	18 9

TABLE II

Ions	$\bar{X}$
Na	3 7
K	13 1
Ca^{++}	10 4
Sr^{++}	20.2
Ba^{++}	31 6
Mg^{++}	2 9
Zn^{++}	13.5
NH	13 3

TABLE III

No.	Compound	X	$\bar{X}$	$\bar{X}$ f T rt te on
1	T rtaric acid $(CHOH)_2(COOH)_2$	4607	60 1	63.2
•	Hydrogen Ammonium T rtrate $NH_4(CHOH)_2(COO)_2H$	4707	8 0	0 6
3	Sodium Tartrate $Na_2(CHOH)_2(COO)_2 \cdot 2H_2O$	4100	87 1	66 7
4	Potassium Tartrate $K_2(CHOH)_2(COO)_2 \cdot \frac{1}{2}H_2O$	4085	96 0	63 3
5	Strontium T rtrate $Sr(CHOH)_2(COO)_2 \cdot 4H_2O$	.6095	138 8	67 0
6	Calcium Tartrate $Ca(CHOH)_2(COO)_2 \cdot 4H_2O$	4077	1 1 6	59.3
⁼	Magnesium Tartrate $Mg(CHOH)_2(COO)_2 \cdot 5H_2O$	5069	13 8	64.5
8	Zinc Tartrate $Zn(CHOH)_2(COO)_2 \cdot 2H_2O$	4*98	107.2	6 7

DISCUSSIONS

The conventional way of representing tartaric acid is which makes it a dihydroxy succinic acid Mean susceptibility $\bar{\chi}$ of succinic acid has been measured by Gray and Birse (1914) which is -54.6×10^{-6} Thus adding the diamagnetic contribution of two oxygens -9.22 10^{-6} to it we get for tartaric acid $\bar{\chi}=-63.8\times10^{-6}$ whereas the experimental value is $-69\ 1\times10^{-6}$ Pascals additive value differentiating two kinds of oxygens [(i) which are singly bounded to carry two atoms and (ii) which are doubly bounded to a single carbon atom] for tartaric acid is -66.7×10^{-6}

For the tartrate ion in the various compounds studied $\bar{\chi}$ varies from $-59\ 0\times10^{-6}$ to $08\ 0\times10^{-6}$ whereas Pascals additive valu is $-60\text{-}9\times10^{-6}$ Thus the diff rent environmental conditions in tartrate ions in these salts produces d formation of the tartrat ion in the crystal lattice which influences th diamagnetism of the ion considerably

The two alkali salts, potassium nd sodium tartrates make a good comparative study of this influence of this deformation on diamagnetism of the radical. From Raman spectra of these two salts (Padmanabhan 1948) it is known that for K-salt the C-H oscillations give one intense line at 2938 Cm^{-1} whereas sodium salt gives two intense lines at 2935 and 2961 Cm^{-1} The splitting of the (C-H) oscillations into two lines n sodium salt is due to the deformation of the tartate ion in sodium salt On referring to table III we also find that th deformation in sodium salt has actually increased the diamagnetism of th tartrate in the salt which is also th case as found in Arrogonite

It will be seen f om tabl III that Pascal's additive val e for tatrate ion $-60\ 7\times10^{-6}$ is very nea to the valu $-59\ 0$ 10^{-6} for tartrate ion in Cal ium salt. But this has no significance Because we can nev r xpect the value of $\bar{\chi}$ for tartrat to be exactly equal to Pascal' law th C-H or O=C oscillations will never be identical in all the salts of t rtaric acid and hence Pascal's constitutive correction will be of different for diff rent salts.

Th work was carried out in th Physical Laboratories, Birla
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